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(F-756CON)



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Jean-Pierre Dath et al.

Confirmation No.: 2790

Serial Number: 10/719,267

Filing Date: November 21, 2003

Title: Production of Olefins

Group Art Unit: 1764

Examiner: Thuan D. Dang

Customer Number: 25264

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**APPEAL BRIEF**

This is an appeal from the decision of the Primary Examiner in the Final Rejection dated April 14, 2006, finally rejecting claims 1 – 3, 5 – 14 and 16 – 35. This Brief is submitted with the statutory fee of \$500.00.

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02 FC:1252 450.00 OP

**Real Party in Interest**

The real party in interest is Total Petrochemicals Research Feluy, successor in name to Fina Research, S.A., a Delaware corporation, as recorded by the assignment filed August 2, 2000.

### Related Appeals and Interferences

Parent Application Serial No. 09/594,059 was the subject of an appeal as noted below. Commonly-assigned applications having the same inventive entity as this application and directed to catalytic cracking processes were the subject of appeals as indicated below.

Application Serial No. 09/594,059 Abandoned

Application Serial No. 09/206,210; now Patent No. 6,713,658

Application Serial No. 09/205,559, Abandoned

Application Serial No. 09/206,207; now Patent No. 6,645,175

Application Serial No. 09/206,208; now Patent No. 6,646,176

Application Serial No. 09/206,218; now Patent No. 6,951,968

Application Serial No. 09/206,216; now Patent No. 7,087,155

Application Serial No. 09/596,356, Abandoned

Copies of the Decisions in the aforementioned appeals are attached in the Related Proceedings Appendix.

### Status of Claims

The claims pending in this application are 1 – 3, 5 – 14 and 16 – 35. Claims 1 – 3, 5 – 14 and 16 – 35 are appealed and are reproduced in the Claims Appendix. No claim is allowed.

### Status of Amendments

No amendment has been filed subsequent to the final rejection.

### Summary of the Claimed Subject Matter

The invention called for in the claims on appeal involves, in its simplest embodiment, the cracking of an olefin-rich hydrocarbon feedstock containing 10 – 100 weight percent olefins in the presence of hydrogen which is added to the feedstock to produce a product having a similar overall olefin content, within  $\pm 15\%$  of the olefin content of the feedstock, but a different olefin distribution. The feedstock is supplied along with hydrogen added to the feedstock to a reactor containing a crystalline silicate catalyst to cause cracking of the feedstock olefins to produce lighter (lower molecular weight) olefins. The catalyst is preferably a crystalline silicate of the MFI family (p. 14, lines 31-35). The MFI crystalline silicates are described in terms of crystal structure and silica/alumina ratios in the specification at page 15, line 1, through page 18, line 1. Preferred MFI silicates are silicalite having silica ratios of 300-500 or more specifically 300-480. (page 15, lines 24-25; page 17, line 34, through page 18, line 1)

The hydrogen added to the feedstock functions to retard the formation of dienes which would lead to the formation of coke resulting in deactivation of the catalysts with an increase in the cycle time between successive catalyst regenerations (p. 9, lines 11-35). The effluent from the reactor preferably contains propylene in an amount within the range of 30-50 wt.% of the total olefin content of the feedstock (p. 16, lines 27-33). The presence of hydrogen, in addition to substantially increasing the cycle time between successive regenerations, also controls the amount of propylene relative to the total  $C_3$  species present. Thus, at low hydrogen partial pressures of up to 5 bar, the propylene purity is high. At a high hydrogen partial pressure, such as 15 bar, the propylene purity is poor. (p. 23, lines 29-35). Desirably, the hydrogen partial pressure is limited to no more than 7.5 bar. (p. 23, line 22 – p. 24, line 6)

The diene content in the feed stream to the cracking reactor can be limited to a maximum of 0.1 wt.% through a preliminary hydrogenation process. (page 25, lines 11-15) This is shown in Figure 1 and the description found in the specification at pages 24-25. The olefin-rich feedstock is supplied through heat exchangers 18 and 8 to cracking reactors 4 and 6. Hydrogen is supplied through an inlet 16 to cause selective hydrogenation of dienes in the hydrogenation reactor 20 to arrive at the requisite low diene content. Olefins are recovered through fractionation columns 26-30 shown in Figure 1, as described at page 25, lines 16-23.

In a preferred embodiment of the invention, ethylene is added to the feedstock containing  $C_{4+}$  olefins prior to introducing the feedstock into the cracking reactor. This may be coupled with the introduction of  $C_{5+}$  olefins to the feedstock. This mode of operation is shown in Figure 5 and described in the specification at page 29, line 24 to page 31, line 8. In Figure 5, the feed stream with hydrogen added is supplied to cracking reactors 54 and 56. The output is supplied to a separator 72 which takes  $C_2$  hydrocarbons, including ethylene, and hydrogen overhead with the  $C_{3+}$  hydrocarbons withdrawn via line 84. The overheads, after a purge to remove methane and ethane, are supplied to a compressor 78, the output of which, including hydrogen and ethylene, is recycled to the feedstock via line 80.  $C_{5+}$  hydrocarbons, including paraffins and olefins, are withdrawn from a separation system via line 96. After removal of some of the  $C_{5+}$  species including paraffins,  $C_5$  olefins are supplied to the feed stream via line 100.



### Prior Art

The prior art references relied upon in rejecting the claims under 35 U.S.C. § 103 are set forth below.

EP 344,444 to Haag et al

EP 109,060 to Colombo et al

### Grounds of Rejection to be Reviewed on Appeal

The grounds of rejection presented are:

Claims 1 – 3, 5, 12, 13, 16 – 25 and 30 under 35 USC 103(a) as obvious over Haag et al.

Claims 6 – 11, 14, and 26 – 29 and 31 – 35 as are unpatentable under 35 U.S.C. § 103(a) over Haag et al in view of Colombo et al.

### Grouping of Claims

In the arguments presented in this Brief, the claims do not stand or fall together. In addition to the arguments applicable to all of the claims rejected over Haag, additional arguments are presented separately with respect to claims 2, 3, 23, and 24; claim 5; claims 16 and 17; claim 21; and claims 22 and 25.

With respect to the claims rejected under 35 U.S.C. § 103 over Haag in view of Columbo, in addition to arguments applicable to all of these claims, additional arguments are presented separately for claims 6, 8, and 26; claims 7 and 28; claim 14; claims 9 and 27; claim 29; claims 30-33, and claim 35.

### Appellants' Arguments

As noted previously under Related Appeals and Interferences, the parent application Serial No. 09/594,059 was the subject of an appeal to the Board of Patent Appeals and Interferences. As indicated in the Decision on Appeal in Serial No. 09/594,059 submitted in the Related Proceedings Index, two of the rejections involved there, based upon Haag under 35 USC 103, or Haag in view of Colombo under 35 USC 103 were affirmed in the Board's Decision. The claims on appeal here are substantially different from those considered in parent application Serial No. 09/594,059. The claims here specify that the feedstock supplied to the catalyst contains 10 – 100 weight percent olefins and further recites that hydrogen is added to the olefin feedstock prior to the contact of the feedstock with the catalyst in the reaction zone.

To the extent that the arguments presented below are similar to those made in the appeal of parent application Serial No. 09/594,059, the specific recitation of a minimum of olefin content of 10 weight percent (or 50 weight percent in claims 22, 30 and 35) together with the specific recitation of adding hydrogen to the feedstock prior to introducing the feedstock into the reaction zone, frames the issues of obviousness in a substantially different manner than those issues considered in the previous appeal.

The rejection of claims 1 – 3, 5, 12, 13, 16 – 25 and 30  
under 35 USC 103(a) as obvious over Haag et al. (EP0034444)

A requirement in all of the claims on appeal is that hydrogen is supplied to the reaction zone by incorporating the hydrogen into the feedstock prior to introduction of the feedstock into the reaction zone. As discussed below, the patent to Haag does not disclose the cracking of an olefin-rich feedstock in the presence of hydrogen to enhance the stability of the catalyst as involved in appellants' invention. Further, the reference in Haag to hydrocracking does not

import into Haag a disclosure of the cracking of olefins in the presence of hydrogen for any purpose. However, even if one were to assume the contrary, it is evident that there is no disclosure in Haag of introducing hydrogen into an olefin-rich feedstock prior to contact of an olefin-rich feedstock with the catalyst. The hydrocracking referred to in Haag would not involve an olefin-rich feedstock of any character, but even if the contrary were to be assumed, there would be no reason, following the teachings of Haag, to introduce hydrogen into the feedstock prior to supply of the feedstock to the reaction zone and into contact with the catalyst.

Assuming that the Haag process were to involve the introduction of hydrogen into the reaction zone, as specifically acknowledged on page 2 of the Final Rejection, Haag is silent as to how or why the hydrogen is added to the reaction zone. If we are to assume that the Haag process involves the addition of hydrogen to the reaction zone containing an olefin-rich feedstock, and this is not found in the Haag reference itself but only in the analysis by the Examiner of what Haag means by the hydrocracking of petroleum products, there is no teaching in Haag of adding the hydrogen to the feedstock prior to supplying the feedstock to the reaction zone.

Common to the rejection of all of the claims in this case, whether based upon Haag alone or Haag in view of Colombo, is the Examiner's position that the reference in Haag to "hydrocracking" involves the cracking of olefins in the presence of hydrogen. The Haag reference contains no such disclosure. Haag is directed to a process for contacting a zeolite catalyst with water in order to enhance its activity. As disclosed in Haag in the abstract and at pages 21-24, the enhanced activity zeolites can be employed in hydrocarbon conversion processes including cracking, hydrocracking, alkylation, dealkylation, transalkylation, isomerization, dimerization, oligomerization, polymerization, disproportionation, and

aromatization. Haag does not disclose the cracking of an olefin-rich feedstock in the presence of hydrogen to produce a lower molecular weight effluent while enhancing the stability of the catalyst. Recognizing this deficiency in Haag, the Final Rejection relies upon the disclosure in Haag of “hydrocracking” as amounting to a disclosure of the cracking of olefins in the presence of hydrogen. However, this interpretation of Haag is not consistent with what one of ordinary skill in the art would understand to be a hydrocracking process. The term “hydrocracking” is commonly understood to be the cracking of petroleum or petroleum products in the presence of hydrogen. Petroleum and petroleum products do not involve material amounts of olefins but are understood by those skilled in the art to involve paraffinic (paraffins and cycloparaffins) and aromatic hydrocarbons. While olefins can be derived from petroleum fractions by refining operations, for example, by conversion of alkanes originally found in petroleum to alkenes, they are not typically present in petroleum or petroleum fractions which are commonly understood to be the feedstock in a hydrocracking procedure. Moreover, even if minor amounts of olefins were to be involved, they would not normally be present in an amount of 10 wt.% or more. Thus, the reference in Haag to “hydrocracking” would not denote to one of ordinary skill in the art the cracking of an olefin-rich hydrocarbon feedstock containing 10 – 100 wt.% olefins as required in the claims. It is again emphasized that hydrocracking processes, as they are understood by those skilled in the art, do not involve the cracking of an olefin-rich feedstock. Far from being rich in olefins, the feedstocks commonly employed in hydrocracking procedures typically involve feedstocks or petroleum fractions, which simply do not involve olefins, much less involving olefin-rich feedstocks having 10 wt.% or more of olefins, or in the case of claims 22, 30 and 35 at least 50 weight percent olefins.

Haag does not disclose the cracking of an olefin-rich feedstock to which hydrogen has been added over a zeolite catalyst to produce a lower molecular weight effluent. Further, Haag fails to disclose that the effluent and the feedstock have olefin contents within the range of  $\pm 15\%$  as recited in all of the claims on appeal. To the extent that the rejection is based upon a presumption that these features or other features called for in applicants' claims are inherent in or must be found in Haag, applicants would respectfully submit that the Examiner has not established any basis for such a presumption. First of all, Haag, as noted above, discloses a wide variety of processes. While hydrogen may be present in some processes (generally Haag refers to hydrogen/hydrocarbon ratios varying from 0, *i.e.* no hydrogen, up to about 20), Haag does not disclose the use of hydrogen in conjunction with the cracking of olefins to lower molecular weight olefins. In fact, the only disclosure of the use of hydrogen in conjunction with olefins appears to be in conjunction with olefin polymerization (the first full paragraph of page 22) or olefin or paraffin aromatization (the paragraph bridging pages 22 and 23). Other processes in which hydrogen may be present involve hydrocracking, isomerization, and disproportionation. These processes obviously do not involve the cracking of higher molecular weight olefins to lower molecular weight olefins. As noticed previously, the term "hydrocracking," as commonly used and as used in the Haag reference, does not involve in any fashion the cracking of an olefin-rich hydrocarbon feedstock in the presence of hydrogen. Further, there is nothing in Haag which would even remotely suggest the use of hydrogen to enhance the stability of the catalyst.

The Final Rejection is in error in its assertion in page 2 that Haag discloses cracking of an olefinic feedstock in the presence of hydrogen in the Abstract or in the material at page 20, line 22, through page 21, line 17, and page 23, line 5 – 26. The abstract simply refers to the main thrust of the Haag disclosure, the use of water to increase catalytic activity, and then concludes

with a laundry list of conversion processes as noted previously. The first portion of this material, page 20, line 22, through page 21, line 11, is not concerned with an olefin cracking procedure. This paragraph appears generally to relate to acid-catalyzed hydrocarbon conversion processes. Beyond this, it is impossible to tell what conversion reactions are referred to here, but at least insofar as olefins are concerned, since the only reference in Haag to the use of hydrogen in connection with olefins is in polymerization or aromatization, it is clear that this material is not applicable to an olefin cracking process. The material in the next paragraph of Haag starting at page 21, line 12, refers to cracking activity in the conversion of a list of materials including olefins. However, hydrocracking or the use of hydrogen would not be involved here. This is evident from the following sentence in Haag which starts: “The activated catalysts produced by the instant invention may also be used in hydrocracking, alkylation . . .” (Emphasis added). Thus, Haag discloses here, cracking which may involve a number of feedstocks including olefins and, separate from this, other processes including hydrocracking. As recognized in page 3 of the Final Rejection, Haag does not disclose the olefin content of the feedstock as set forth in each of independent claims 1, 22 and 30. The comments found here as to what one of ordinary skill in the art would “expect” does not address the issue presented by a rejection under 35 USC 103. The issue under 35 U.S.C. § 103 is one of obviousness of the claimed subject matter to one of ordinary skill in the art. Such obviousness cannot be established by a mere assertion of obviousness. Similarly, obviousness cannot be established by a mere assertion that feedstocks containing any amount of olefins would yield similar results. There is simply no basis in the prior art of record in this application to support the Examiner’s position taken here. A mere assertion of obviousness, without factual support in the prior art as to why the invention is

considered to be obvious, is not sufficient to support a rejection under 35 U.S.C. §103. Thus, in *In re Cofer*, 148 USPQ 268 (CCPA 1966), the court stated at page 271:

“Necessarily it is facts – which must support the legal conclusion of obviousness under 35 U.S.C. § 103. Merely stating that a compound or composition is obvious, without adequate factual support, is not sufficient.”

Here, as in *In re Cofer*, the rejection based upon Haag amounts simply to a statement that the invention is obvious without giving facts other than those found in applicants’ specification, in support of this conclusion.

Attention is also respectfully invited to MPEP § 2143.01 (Rev 3, 2005), which states in the third paragraph:

“Obviousness can only be established by combining or modifying the teachings of the prior art to produce the claimed invention where there is some teaching, suggestion, or motivation to do so found either explicitly or implicitly in the references themselves or in the knowledge generally available to one of ordinary skill in the art.”

Here, the only basis for modifying the reference to provide cracking of an olefin-rich feedstock containing from 10-100 wt.% olefins is found in applicants’ specification and not in the prior art. The material found in Haag at page 23, lines 5-26, refers to two different types of conversion, cracking in lines 5-15 and hydrocracking in lines 15-26. As noted previously, hydrocracking is carried out with respect to petroleum fractions involving saturated aliphatic compounds and aromatic compounds. Hydrocracking is not commonly understood to involve a process involving the cracking of olefin-rich feedstocks.

In regard to claims 2 and 3 and 23 and 24, appellants respectfully submit that the claimed hydrogen partial pressures cannot be found in Haag since, as noted above, Haag clearly does not

disclose the use of hydrogen in an olefin cracking process. Hydrocracking is, of course one of many reactions disclosed in Haag, and as noted above, hydrocracking does not involve the cracking of an olefin-rich feedstock containing 10-100 wt.% olefins. With respect to the olefin partial pressures found in claims 18 and 19 or the temperatures found in claims 16 and 17, appellants would respectfully submit that the very broad ranges found in Haag, and even then not in respect of an olefin cracking process, do not anticipate or render obvious the very narrow ranges, such as the temperature range of 540-580°C set forth in claim 17. In regard to the disclosure in Haag of a range of about 400°F (204.4°C) to about 1000°F (537.7°C), it is noted that this range is further characterized as “preferably from about 500°F (260°C) to about 850°F (454.4°C). Both of the ranges disclosed in Haag are below applicants’ range, and the upper limit of this preferred range in Haag is far below the preferred range of 540-580°C involved in applicants’ process. Thus, Haag not only fails to disclose or render obvious appellants’ range of 540-580°C, but also Haag actually teaches away from this range and the broader range of 500-600°C. With regard to this claim and other claims in which the Examiner takes the position that a very broad range found in the prior art would necessarily anticipate or render obvious a narrow encompassed range called for in a claim, attention is respectfully invited to Section 2131.03 MPEP, page 2100-80 (Rev. 3, 2005):

When the prior art discloses a range which touches, overlaps or is within the claimed range, but no specific examples falling within the claimed range are disclosed, a case by case determination must be made as to anticipation. In order to anticipate the claims, the claimed subject matter must be disclosed in the reference with “sufficient specificity to constitute an anticipation under the statute.” What constitutes a “sufficient specificity” is fact dependent. If the claims are directed to a narrow range, the reference teaches a broad range, and there is evidence of unexpected results within the claimed narrow range, depending on the other facts of the case, it may be reasonable to conclude that the narrow range is not disclosed with



“sufficient specificity” to constitute an anticipation of the claims.  
The unexpected results may also render the claims unobvious.

It would appear that the Final Rejection fails to consider this practice as outlined in § 2131.03. Instead, the position taken in the Final Rejection simply involves a broad assertion of obviousness without any reasoning in support of this position.

In addition to the reasons advanced above, appellants would respectfully submit that dependent claims 5, 12, 13, and 21 recite additional limitations which further establish patentability of these claims over the patent to Haag. Claim 5 specifies that at least part of the hydrogen employed in the cracking process is recycled from the effluent produced in the cracking process. Clearly, there is nothing in Haag that would render obvious the recycle of hydrogen as specified in claim 5. With respect to claim 5 and also claims 12 and 13, applicants would respectfully submit that the issue of unobviousness must be determined by consideration of what is found in the prior art, and against this background, applicants would respectfully submit that a mere assertion of obviousness without factual support is not sufficient to support a rejection under 35 U.S.C. § 103. In this regard, attention is respectfully invited to the previous reference to *In re Cofer* and MPEP § 2143.0.

Necessarily it is facts . . . which must support the legal conclusion of obviousness under 35 U.S.C. § 103. Merely stating that a compound or composition is obvious, without adequate factual support, is not sufficient.

With respect to the arguments regarding optimization the paragraph at the top of page 4 and on page 6 of the Final Rejection, appellants would respectfully submit that the issue presented under 35 U.S.C. § 103 is not one of optimization, but one of obviousness to one skilled in the art. As stated in MPEP § 2144.05II(B), under the heading, “Only Result-Effective Variables can be Optimized”:

A particular parameter must first be recognized as a result-effective variable, *i.e.*, a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation.

The simple fact is that there is nothing in the prior art references to support the proposition that only the routine experimentation of a prior art recognized result-effective variable is involved. Further, appellants would respectfully submit that the Examiner has provided no basis in the prior art for the position taken regarding the optimization of the cost of raw materials.

With respect to claim 21, as acknowledged on page 4 of the Final Rejection, Haag does not even address the subject of dienes. The fact that Haag fails to discuss the significance of the diene concentration of the feedstock does not in itself provide a basis for a finding that it would be obvious to remove dienes from such a feedstock. In any event, as is noted previously, Haag clearly is not at all concerned with the cracking of an olefin-rich feedstock in the presence of hydrogen.

Further with respect to this and other issues which the Final Rejection fails to address, but instead relies upon the proceedings in the parent application, appellant's would again note that the claims here and the issues presented in this appeal are significantly different than those in the parent application. As to the subject of the disclosure found in page 5, lines 19 – 30 of applicant's original specification, this material was cancelled in the Preliminary Amendment attendant to filing of this application, thus, avoiding any inference of an admission as discussed in more detail in the remarks accompanying the Preliminary Amendment. It is respectfully submitted that rejections here should be considered with a view to the claims and disclosure as found in this application and not in the parent application.

The rejection under 35 USC 103(a) of claims 6-11, 14, 26-29,  
and 31-35 as unpatentable over Haag in view of Colombo

It is noted that the proposed combination of references, even if made exactly as proposed in the Final Rejection, does not cure the deficiency observed above with respect to the use of hydrogen. Colombo, like Haag, does not disclose the cracking of an olefin-rich feedstock in the presence of hydrogen. In reference to claims 10 and 11, appellants would respectfully submit that the proposed combination of Haag and Colombo to arrive at the use of silicalite or a catalyst having a silicon/aluminum atomic ratio of at least 180 can be made only with the benefit of a hindsight after reviewing applicants' disclosure. It will be recalled that Haag discloses the use of a large number of ZSM zeolites which have relatively low silica/alumina mole ratios. Haag in pages 5 and 6 calls for the use of zeolites having a silica/alumina mole ratio of at least about 12 and specifies that it is preferred to use zeolites having higher ratios of at least about 30. Haag goes on to exemplify such higher silica/alumina ratios as being "about 70" (page 28, line 28, and page 32, line 24) and gives further examples, such as in Example 15 which can be calculated to be about 53. These are all silica/alumina mole ratio which must be divided by 2 to arrive at the silicon/aluminum atomic ratio. Thus, the highest ratio in terms of the silicon/aluminum ratio appears to be a calculated ratio of 35 as found in Examples 4 and 8. Against this teaching in Haag, applicants would respectfully submit that to replace the Haag zeolites with silicalite or other molecular sieves having a silicon/aluminum atomic ratio of at least 180 would be possible only in hindsight after a consideration of appellants' disclosure. One of ordinary skill in the art would not, viewing only the Haag and Colombo references, attempt to replace the zeolites in Haag which have appreciable aluminum contents with the silicalites in Colombo which have no aluminum content, *i.e.* a silicon/aluminum ratio of infinity

With respect to claims 6-9 and 26-29, appellants note the comments found on page 5 of the Final Rejection that ethylene and other high olefins are present in the product of the Colombo patent. However, appellants' claims specify the addition of ethylene to the feedstock, and this clearly is not disclosed in either Haag or Colombo. In regard to the material found at page 3, lines 28-30, of Colombo, this appears to be a negative teaching in Colombo. This paragraph starting on line 18 of page 3 and carrying over to page 4 actually involves the disclosure of a process incorporating an oligomerization step in order to avoid recycle of C<sub>4</sub> olefins unreacted or formed during the reaction. Further, appellants would respectfully note that such olefins would by no means necessarily include ethylene. In any case, there is nothing in the references which would render obvious the recycle of ethylene to the feedstock as required in claims 7 and 28. Further, the proposed combination of references would not lead one of ordinary skill in the art to the separation and recycle procedure of claim 28 involving, in addition, the recycling of C<sub>5</sub> olefins to the feedstock.

In regard to appellants' dependent claim 14 and also independent claim 31, it is noted that Colombo does not disclose a propylene yield on an olefin basis of 30-50% based on the olefin content of the feedstock. As shown in Fig. 1 of Colombo, the propylene is necessarily substantially less than 30% based upon the conversion data and the selectivity to propylene data presented in Fig. 1. To the extent that Table 4 of Colombo may be relied upon, the average propylene yield across the six examples reported there would appear to be well below a propylene yield on an olefin basis of 30%. If one of ordinary skill in the art were to attempt to modify the teachings of Haag to provide certain propylene yields based upon the data shown in Table 4, the results would be propylene yields less than 30%, similar to the data presented in Fig. 1 of Colombo. Further, appellants would respectfully submit that the question posed under 35

U.S.C. § 103 is not whether one of ordinary skill in the art could selectively pick out portions of the references in an attempt to combine them after reading appellants' disclosure. Instead, the issue is whether one of ordinary skill in the art would find the claimed process obvious in view of the prior art without the benefit of hindsight afforded by referring to appellants' disclosure.

In addition to the distinctions discussed above with respect to Haag or Haag combined with Colombo, appellants would respectfully refer to the following claims which, as discussed below, recite subject matter not rendered obvious in view of the prior art references.

Claim 25 further specifies that the olefin content of the effluent is  $\pm 10\%$  of the olefin content of the feedstock. Claim 26 calls for the feedstock to contain olefins of 4 or more carbon atoms and, as discussed previously, further recites that ethylene is added to the feedstock prior to its introduction into the reaction zone. Claim 27 depends from claims 26 and specifies that a stream of C<sub>5</sub> or greater olefins are added to the feedstock prior to its introduction to the reaction zone.

Claim 28 is directed to the procedure shown in appellants' Fig. 5 and the attendant text at page 30, line 27, through page 31, lines 7, in which the effluent from the reaction zone is applied to a separation zone to recovery a light fraction of ethylene and a heavier fraction of C<sub>3</sub>-C<sub>5</sub> olefins, with recycle of the ethylene and the C<sub>5</sub> olefins to the feedstock. Claim 29 depends from claim 28 and specifies that the ethylene recycled to the feedstock contains hydrogen. No matter what construction one might place on the Haag hydrocracking procedure, this subject matter is not found in or rendered obvious by the prior art. The reference in the Final Rejection to *In re Marsheck*, 168 USPQ 721 is noted. However, the decision there is obviously fact-intensive based upon the claimed subject matter and the prior art involved in that case and has no applicability to the situation here.

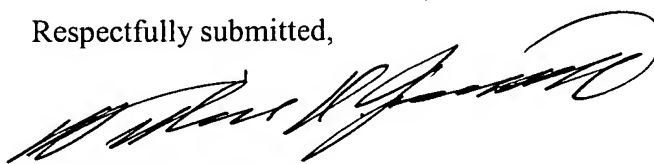
Claims 31 and 32 depend from claim 30 and specify an MFI-type catalyst having a silicon/aluminum atomic ratio within the range of, respectively, 300-500 and 300-480. The prior art references, no matter how combined, would not result in the use of an MFI-type catalyst having a silicon/aluminum atomic ratio within the relatively narrow confines called for in these claims.

### Conclusion

For the reasons set forth above, Appellants respectfully submit that all of the claims herein are patentable over the prior art. Accordingly, it is respectfully requested that the Final Rejection of the claims be reversed.

Enclosed is a check in the amount of \$950.00 to cover the \$500.00 fee for the filing of this Appeal Brief, and \$450.00 to cover a two-month extension fee. The Commissioner is hereby authorized to charge any additional fee that may be due in connection with this Appeal Brief or to credit any overpayment to Deposit Account No. 50-2225.

Respectfully submitted,



William D. Jackson  
Registration No. 20,846

November 15, 2006

Schultz & Associates, P.C.  
One Lincoln Centre  
5400 LBJ Freeway, Suite 1200  
Dallas, Texas 75240  
Telephone: 214/210-5931  
Facsimile: 214/210-5941

## Claims Appendix

1. A process for cracking an olefin-rich hydrocarbon feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing olefins in an amount within the range of 10 to 100 wt.% having a first composition of one or more olefinic components with a crystalline silicate catalyst to produce an effluent having a second composition of one or more olefinic components in which the olefin distribution is different from the olefin distribution of said feedstock, the feedstock and the effluent having substantially the same olefin content by weight therein wherein the olefin content of the effluent is within  $\pm 15\%$  of the olefin content of the feedstock, adding hydrogen to the olefin-rich feedstock prior to contact of said feedstock with said crystalline silicate catalyst to provide for the olefin-rich feedstock contacting the catalyst in the presence of hydrogen for enhancing the stability of the catalyst.

2. A process according to claim 1 wherein the hydrogen partial pressure is up to 7.5 bar.

3. A process according to claim 2 wherein the hydrogen partial pressure is from 0.1 to 5 bar.

5. A process according to claim 1 wherein at least a part of the hydrogen is recycled from the effluent.

6. A process according to claim 1 wherein ethylene has been added to a C<sub>4</sub><sup>+</sup> hydrocarbon feedstock.

7. A process according to claim 6 wherein at least a part of the ethylene is recycled from the effluent.

8. A process according to claim 6 wherein the ethylene comprises from 0.1 to 50 wt.% of the hydrocarbon feedstock.

9. A process according to claim 6 further comprising recycling at least a part of C<sub>5</sub> or greater olefins from the effluent to the feedstock.

10. A process according to claim 1 wherein the catalyst comprises silicalite.

11. A process according to claim 1 wherein the catalyst has a silicon/aluminum atomic ratio of at least 180.

12. A process according to claim 1 wherein the feedstock comprises a light cracked naphtha.

13. A process according to claim 1 wherein the feedstock comprises a C<sub>4</sub> cut from a fluidised-bed catalytic cracking unit in a refinery, or a C<sub>4</sub> cut from a unit in a refinery for producing methyl tert-butyl ether or a C<sub>4</sub> cut from a steam-cracking unit.

14. A process according to claim 1 wherein the catalytic cracking has a propylene yield on an olefin basis of from 30 to 50% based on the olefin content of the feedstock.



16. A process according to claim 1 wherein the feedstock contacts the catalyst at an inlet temperature of from 500 to 600 °C.

17. A process according to claim 16 wherein the inlet temperature is from 540 to 580 °C.

18. A process according to claim 1 wherein the feedstock contacts the catalyst at an olefin partial pressure of from 0.1 to 2 bar.

19. A process according to claim 18 wherein the olefin partial pressure is around atmospheric pressure.

20. A process according to claim 1 wherein the feedstock is passed over the catalyst at an LHSV of from 10 to 30 h<sup>-1</sup>.

21. A process according to claim 1 wherein the feedstock has a maximum diene concentration therein of 0.1 wt.%.

22. A process according to claim 1 wherein said feedstock contains 50 wt.% olefins.

23. A process for cracking an olefin-rich feedstock which is selective to light olefins in the effluent, comprising:

supplying an olefin rich hydrocarbon feedstock containing from 10 to 100 wt.% olefins into a reaction zone which contains a crystalline silicate catalyst of the MFI family which is effective for the cracking of the olefins;

supplying hydrogen to said reaction zone at a hydrogen partial pressure of not more than 7.5 bar whereby hydrogen is added to the olefin-rich feedstock prior to supplying said olefin-rich feedstock into said reaction zone to provide that the olefin-rich feedstock contacts the catalyst in the presence of hydrogen to enhance the stability of the catalyst;

operating of said reaction zone at temperature and pressure conditions effective to cause cracking of olefins in said feedstock to produce olefins which are lighter than olefins in the feedstock; and

recovering an effluent from said reaction zone which has an olefin content by molecular weight within  $\pm 15\%$  of the olefin content of the feedstock and which has a lower average molecular weight than that of the olefin content of the feedstock.

24. The process according to claim 23 wherein the hydrogen partial pressure is within the range of 0:1 to 5 bar.

25. The process of claim 23 wherein said effluent has an olefin content which is within  $\pm 10\%$  of the olefin content of the feedstock.

26. The process of claim 23 wherein said feedstock contains olefins having four or more carbon atoms and wherein ethylene is added to the feedstock prior to the introduction of said feedstock into said reaction zone.

27. The process of claim 26 wherein a stream of C<sub>5</sub> or greater olefins is added to the feedstock prior to the introduction of the feedstock into the reaction zone.

28. The process of claim 23 further comprising supplying said effluent to a separation zone and operating said separation zone to recover a light fraction containing ethylene and a heavier fraction containing C<sub>3</sub> – C<sub>5</sub> olefins, recycling ethylene in said light fraction to the feedstock prior to the introduction of the feedstock into the reaction zone and recycling C<sub>5</sub> olefins in said heavier fraction to said feedstock prior to the introduction of said feedstock into said reaction zone.

29. The process of claim 28 wherein the ethylene recycled to said feedstock contains hydrogen.

30. A process according to claim 23 wherein said feedstock contains 50 wt.% olefins.

31. A process for cracking an olefin-rich feedstock which is selective to light olefins including propylene in the effluent, comprising:

supplying an olefin rich hydrocarbon feedstock containing from 10 to 100 wt.% olefins and containing one or more olefins of C<sub>4</sub> or greater into a reaction zone containing a crystalline silicate catalyst which is effective for the cracking of the olefins;

supplying hydrogen to said reaction zone at a hydrogen partial pressure of not more than 7.5 bar whereby hydrogen is added to the olefin-rich feedstock prior to supplying said olefin-rich feedstock into said reaction zone to provide that the olefin-rich feedstock contacts the catalyst in the presence of hydrogen to enhance the stability of the catalyst;

operating said reaction zone at temperature and pressure conditions effective to cause cracking of olefins in said feedstock to produce olefins which are lighter than olefins in the feedstock and to produce a propylene yield within the range of 30 to 50 wt.% based on the olefin content of the feedstock; and

recovering an effluent from said reaction zone which has an olefin content by weight within  $\pm 15\%$  of the olefin content of the feedstock and which has a lower average molecular weight than that of the olefin content of the feedstock, said effluent containing propylene in an amount within the range of 30 to 50 wt.% of the total olefin content of the feedstock.

32. The process of claim 31 wherein said crystalline silicate catalyst is an MFI-type catalyst having a silicon/aluminum atomic ratio within the range of 300-500.

33. The method of claim 32 wherein said catalyst has a silicon/aluminum atomic ratio within the range of 300-480.

34. The process of claim 31 wherein said reaction zone is operated at an inlet temperature within the range of 500-600 °C and an olefin partial pressure within the range of 0.1–2 bars.

35. The process of claim 31 wherein said feedstock contains greater than 50 wt.% C<sub>4</sub> as an olefin.

**PATENT**

**Serial No. 10/719,267**  
**31223.00020**  
**F-756CON**

**EVIDENCE APPENDIX**

Evidence submitted pursuant to 37 CFR §1.130, 131, 1.132 relied upon by appellant in this appeal: None.

Evidence relied upon by the Examiner in rejecting the claims:

Haag European Patent 0034444 – attached

Colombo et al. European Patent 0109060 – attached

The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

Paper No. 22

UNITED STATES PATENT AND TRADEMARK OFFICE

RECEIVED

JUN 29 2004

BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

~~Ex parte~~ JEAN-PIERRE DATH and WALTER VERMEIREN

MAILED

JUN 24 2004

U.S. PATENT AND TRADEMARK OFFICE  
BOARD OF PATENT APPEALS  
AND INTERFERENCES

Appeal No. 2004-0988  
Application No. 09/596,356

ON BRIEF

Before WARREN, WALTZ, and DELMENDO, Administrative Patent Judges.  
WALTZ, Administrative Patent Judge.

ON REQUEST FOR REHEARING

Pursuant to the provisions of 37 CFR § 1.197(b) (1997), appellants have submitted a Request for Rehearing (hereafter "Request") of our Decision dated March 31, 2004, affirming the examiner's rejection of claims 1 through 9 under 35 U.S.C. § 103(a) as unpatentable over Colombo in view of Haag (Decision, page 3).

Appellants request rehearing based on two points of error (Request, page 1). First, appellants argue that the Board's Decision is in error for finding a *prima facie* case of obviousness based on the Haag teaching of application of the steaming procedure

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Application No. 09/596,356

to catalysts with Si/Al ratios which are inclusive of the claimed ranges (Request, page 2). Appellants argue that, viewing the Haag disclosure in its entirety, one of ordinary skill in the art would come to the "inevitable conclusion" that Haag is dealing with Si/Al atomic ratios well below the 150-800 range required by the claims on appeal (Request, pages 2-3).

Appellants' argument is not well taken. As noted in the Decision at page 3, the examiner finds that Colombo discloses Si/Al atomic ratios well within the claimed range. Even assuming *arguendo* that Haag did not disclose or suggest the claimed Si/Al ratios, Colombo has been applied by the examiner for the disclosure of these claimed ratios. The motivation to apply the steaming procedure of Haag to activate the catalysts of Colombo has been established by the examiner (Decision, sentence bridging pages 3-4; see Colombo, page 3, ll. 9-17). Alternatively, considering the entirety of Haag, one of ordinary skill in the art would not limit this reference to its examples but the open ranges taught by Haag for Si/Al ratios ("at least 12" and "at least about 30") would have suggested the claimed ranges, as well as the applicability of the steaming procedure to the catalysts of Colombo. See the Decision, pages 5-6, where a similar argument by appellants was not persuasive.



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Appellants argue, as the second point of error, that the Decision finds the disclosure in Colombo to "initial activation" to include a reference to the subsequent steaming procedure (Request, pages 3-4). This argument is not persuasive for reasons stated on page 5 of the Decision, where this same argument was answered (see the Brief, page 6). Appellants have not contested or disputed the explanation in the Decision that Colombo and Haag teach that the heating and base exchange merely renders the catalyst active and in the correct (hydrogen or acidic) form for the subsequent steam treatment to increase the catalytic activity (Decision, page 5, with citations to Haag and Colombo).

Finally, appellants argue that claim 6 should be treated as it stands in Exhibit A attached to appellants' Brief since the examiner and appellants treat the amendment mailed Dec. 17, 2002, as having been entered (Request, page 4). This argument is not persuasive since this merits panel has considered the claims on appeal as found in the file record. Upon the return of this application to the jurisdiction of the examiner, the examiner and appellants should clarify the record and insure that all amendments have been correctly entered.

We do not find in the Request any argument convincing us of error in the conclusions we reached in our Decision.

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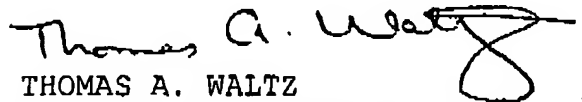
Accordingly, appellants' Request for Rehearing is denied.

No time period for taking any subsequent action in connection  
with this appeal may be extended under 37 CFR § 1.136(a).

**DENIED**



CHARLES F. WARREN )  
Administrative Patent Judge )



THOMAS A. WALTZ )  
Administrative Patent Judge )

BOARD OF PATENT  
APPEALS  
AND  
INTERFERENCES



ROMULO H. DELMENDO )  
Administrative Patent Judge )

TAW/jrg

Appeal No. 2004-0988  
Application No. 09/596,356

FINA TECHNOLOGY INC.  
PO BOX 674412  
HOUSTON, TX 77267-4412

12

**EUROPEAN PATENT APPLICATION**

21 Application number: 81300484.3

22 Date of filing: 05.02.81

51 Int. Cl.3: **B 01 J 29/28**

**C 10 G 11/05, C 07 C 4/06**  
**C 07 C 6/00, C 07 C 5/22**  
**C 07 C 2/54, C 07 C 5/41**  
**C 07 C 2/12, C 10 G 47/16**

30 Priority: 14.02.80 US 121339

43 Date of publication of application:  
26.08.81 Bulletin 81/34

84 Designated Contracting States:  
BE DE FR GB IT NL

71 Applicant: **MOBIL OIL CORPORATION**  
**150 East 42nd Street**  
**New York New York 10017(US)**

72 Inventor: **Haag, Werner Otto**  
**38 Pine Knoll Drive**  
**Lawrenceville New Jersey 08648(US)**

72 Inventor: **Lago, Rudolph Michael**  
**633 Kings Road**  
**Yardley Pennsylvania 19067(US)**

74 Representative: **Cooper, John Anthony et al,**  
**Mobil Court 3 Clements Inn**  
**London WC2A 2EB(GB)**

54 Enhancement of zeolite catalytic activity.

57 A method is provided for increasing the catalytic activity of acid zeolite catalysts characterized by a silica to alumina mole ratio of at least 12 and a constraint index within the approximate range of 1 to 12, comprising contacting said zeolite catalysts with water for a sufficient treating time, temperature and water partial pressure to bring about said increased activity. The increase in catalytic activity is within a zone of enhanced activity, said zone is defined as encompassing all those conditions of treating time, temperature and water partial pressure and combinations thereof which yield catalytic activities greater than initial catalyst activity. The zeolite of enhanced activity of the method of the present invention can be utilized in improved acid catalyzed hydrocarbon conversion processes such as cracking, hydrocracking, alkylation, dealkylation, transalkylation, isomerization, dimerization, oligomerization, polymerization, addition, disproportionation, aromatization and hydration.

EP 0 034 444 A2

0417

ENHANCEMENT OF ZEOLITE CATALYTIC ACTIVITYBACKGROUND OF THE INVENTIONField of the Invention

5 This invention relates to a method for substantially increasing the acid catalytic activity of members of a unique class of crystalline zeolites by treatment with water under controlled conditions.

Description of the Prior Art

10 It is known in the art that the use of steam (water) and/or ammonia can be utilized to modify the activity of acid catalysts, e.g. clays, silica-aluminas and zeolites. Much of the emphasis in the field of catalyst activity modification has been directed towards reducing the activity of catalysts. For example, U.S. Patent No.  
15 4,016,218 teaches the use reduction of catalytic activity of a class of zeolites having a silica to alumina mole ratio of at least 12 and a constraint index within the approximate range of 1 to 12 by the use of prior thermal treatment. Such prior thermal treatment includes the use of a steam  
20 atmosphere. It is also known that the use of ammonia can suppress an initially high activity catalyst.

Hydrogen zeolites of the 1 to 12 constraint index type are generally prepared from their alkyl ammonium and ammonium form precursors by calcining in an inert  
25 atmosphere, usually in nitrogen at about 1000°F. The more costly nitrogen atmosphere is chosen over the cheaper heating in air to avoid temperature runaway and steam

formation that is known to damage the catalyst and results in lower activity. Small samples in the laboratory can be calcined in air without significant steam damage if the temperature is controlled by a slow heat up and by allowing any steam formed to diffuse away. With this careful first calcination, hydrogen zeolites result that are free of residual nitrogen compounds and have the maximum number of acidic hydroxyl group, which is equal to the number of framework aluminums. Samples thusly prepared are designated "fresh samples". The corresponding catalytic activity of these fresh samples is called "initial activity" and when measured by the alpha ( $\alpha$ ) test as described hereinafter, assigned the designation of " $\alpha_0$ ."

It has long been known that the catalytic activity of hydrogen zeolites can be reduced by high temperature heating and especially by steaming.

It is also known that the deactivation due to steam is more pronounced at higher temperatures and longer reaction times. It is also more pronounced at higher steam pressures. Deactivation in the absence of steam, i.e., in an inert atmosphere, requires more severe conditions than steam deactivation.

Recently it has been found that the use of water can be employed to improve certain zeolite catalyst characteristics, while maintaining catalyst activity levels. U.S. Patent Nos. 4,149,960 and 4,150,062 describe the use of

about 0.5 to about 15 moles of water per mole of feedstock in order to substantially reduce the coking and aging rates of the zeolite catalysts used in the processes of these disclosures.

5 U.S. Patent 3,493,519 teaches a method of using steam for the stabilization of Y-faujasite zeolite. There, a chelating agent was used after steaming to take out the excess aluminum from the zeolite. The resultant catalyst of this process is a hydrothermally stable zeolite catalyst  
10 having high hydrocarbon conversion activity.

In U.S. Patent 3,546,100, it is disclosed that a rare earth exchanged zeolite hydrocracking catalyst such as zeolites X or Y can be improved with respect to its cracking activity and selectivity by using water in controlled  
15 amounts to activate catalyst cracking sites. This disclosure states that the amount of water be maintained during the process such that the water vapor partial pressure is kept at a level of about 10 to about 130 mm. water vapor.

20

#### SUMMARY OF THE INVENTION

In accordance with the present invention, there has now been discovered a method for substantially increasing the acid catalytic activity of members of a unique class of zeolites by treatment with water, i.e.  
25 liquid water or steam under controlled conditions. Whereas under prior art methods the activity of a fresh acid zeolite monotonically decreases upon thermal treatment, under the controlled conditions of this invention, there is a

considerable increase in activity over the initial activity.

The members of the unique class of zeolites of the present invention are characterized by a silica to alumina mole ratio of at least 12 and a constraint index within the approximate range of 1 to 12. Unlike other catalyst activation methods, water (steam) addition during the catalytic reaction is not a requirement, rather the catalyst is treated prior to use.

The enhanced zeolite activity attainable by the use of the method of this invention is achieved only under carefully controlled conditions. These conditions depend on the interplay of several variables such as temperature, water partial pressure, treating time, nature of zeolite and nature of treating gas. There exists a "zone of enhanced activity" where zeolite activity is increased over initial activity. Under conditions that are too mild, catalyst activation is not obtained. Alternatively, under too severe conditions, the catalyst will undergo deactivation. Under conditions of constant temperature, the following expression approximately describes the relationships of two variables, treating time and water partial pressure:

$$0.01 (Pt)_T < (Pt) < 10(Pt)_T$$

$$\text{where } (Pt)_T = 2.6 \times 10^{-9} e^{16000/T}$$

P = Water Partial Pressure, atmospheres

t = Treating Time, hours

T = Temperature, °K



Whereas under prior art methods ammonia is used to suppress catalyst activity, under the controlled water treating conditions of the present invention, ammonia addition yields even higher activities than with water treating alone.

#### BRIEF DESCRIPTION OF THE DRAWING

The drawing is a plot of relative activity for n-hexane cracking versus water partial pressure in the calcination of HZSM-5/ $\text{Al}_2\text{O}_3$ .

#### DESCRIPTION OF PREFERRED EMBODIMENTS

The catalyst used in the method described herein comprises a crystalline zeolite which is a member of a class of zeolites exhibiting some unusual properties. These zeolites induce profound transformation of aliphatic hydrocarbons to aromatic hydrocarbons in commercially desirable yields and are generally highly effective in conversion reactions involving aromatic hydrocarbons. Although they have unusually low alumina contents, i.e., high silica to alumina mole ratios, they are very active even when the silica to alumina mole ratio exceeds 30. The activity is surprising since catalytic activity is generally attributed to framework aluminum atoms and cations associated with these aluminum atoms. These zeolites retain their crystallinity for long periods in spite of the presence of steam at high temperature which induces irreversible collapse of the framework of other zeolites, e.g., of the X and A type.

An important characteristic of the crystal structure of this class of zeolites is that it provides constrained access to, and egress from the intracrystalline free space by virtue of having a pore dimension greater than about 5 Angstroms and pore windows of about a size such as would be provided by 10-membered rings of silicon atoms interconnected by oxygen. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline zeolite, the oxygen atoms themselves being bonded to the silicon or aluminum atoms at the centers of the tetrahedra. Briefly, the preferred type zeolites useful in this invention possess, in combination: a silica to alumina mole ratio of at least about 12; and a structure providing constrained access to the intercrystalline free space.

The silica to alumina mole ratio referred to may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with a silica to alumina mole ratio of at least 12 are useful, it is preferred to use zeolites having higher ratios of at least about 30. Such zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water, i.e., they exhibit "hydrophobic" properties. It is believed that this hydrophobic character is advantageous in the present invention.

The type zeolites useful in this invention freely sorb normal hexane and have a pore dimension greater than about 5 Angstroms. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of silicon and aluminum atoms, then access by molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the desired type. Windows of 10-membered rings are preferred, although, in some instances, excessive puckering or pore blockage may render these zeolites ineffective. Twelve-membered rings do not generally appear to offer sufficient constraint to produce the advantageous conversions, although puckered structures exist such as TMA offretite which is a known effective zeolite. Also, structures can be conceived, due to pore blockage or other cause, that may be operative.

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access, a simple determination of the "constraint index" may be made by passing continuously a mixture of an equal weight of normal hexane and 3-methylpentane over a sample of zeolite at atmospheric pressure according to the following procedure. A sample of the zeolite, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the zeolite is treated with a stream of air at 1000°F for at least 15 minutes. The

zeolite is then flushed with helium and the temperature adjusted between 550°F and 950°F to give an overall conversion between 10% and 60%. The mixture of hydrocarbons is passed at a 1 liquid hourly space velocity (i.e., 1 volume of liquid hydrocarbon per volume of zeolite per hour) over the zeolite with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The "constraint index" is calculated as follows:

$$\text{Constraint Index} = \frac{\log_{10}(\text{fraction of n-hexane remaining})}{\log_{10}(\text{fraction of 3-methylpentane remaining})}$$

The constraint index approximates the ratio of the cracking rate constants for the two hydrocarbons. Zeolites suitable for the present invention are those having a constraint index in the approximate range of 1 to 12. Constraint Index (CI) values for some typical zeolites are:

	<u>ZEOLITE</u>	<u>C.I.</u>
	ZSM-5	8.3
	ZSM-11	8.7
	ZSM-12	2
5	ZSM-23	9.1
	ZSM-38	2
	ZSM-35	4.5
	Clinoptilolite	3.4
	TMA Offretite	3.7
10	Beta	0.6
	ZSM-4	0.5
	H-Zeolon	0.4
	REY	0.4
15	Amorphous Silica-Alumina (non-zeolite)	0.6
	Erionite	38

It is to be realized that the above constraint index values typically characterize the specified zeolites but that such are the cumulative result of several variables used in determination and calculation thereof. Thus, for a given zeolite depending on the temperature employed within the aforementioned range of 550°F to 950°F, with accompanying conversion between 10% and 60%, the constraint index may vary within the indicated approximate range of 1 to 12. Likewise, other variables such as the crystal size of the zeolite, the presence of possible occluded contaminants and binders intimately combined with the zeolite may affect the constraint index. It will accordingly be understood by those skilled in the art that the constraint index, as utilized herein, while affording a highly useful means for characterizing the zeolites of interest is approximate, taking into consideration the manner of its determination; with probability, in some instances, of compounding variable extremes.

While the above experimental procedure will enable one to achieve the desired overall conversion of 10 to 60% for most catalyst samples and represents preferred conditions, it may occasionally be necessary to use somewhat more severe conditions for samples of very low activity, such as those having a very high silica to alumina mole ratio. In those instances, a temperature of up to about 1000°F and a liquid hourly space velocity of less than one, such as 0.1 or less, can be employed in order to achieve a minimum total conversion of about 10%.

The class of zeolites defined herein is exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38 and other similar materials. U.S. Patent 3,702,886 describing and claiming ZSM-5 is incorporated herein by reference.

ZSM-11 is more particularly described in U.S. Patent 3,709,979, the entire contents of which is incorporated herein by reference.

ZSM-12 is more particularly described in U.S. Patent 3,832,449, the entire contents of which is incorporated herein by reference.

ZSM-23 is more particularly described in U.S. Patent 4,076,842, the entire contents of which is incorporated herein by reference.

ZSM-35 is more particularly described in U.S. Patent 4,016,245, the entire contents of which is incorporated herein by reference.

ZSM-38 is more particularly described in U.S. Patent 4,046,859, the entire contents of which is incorporated herein by reference.

The specific zeolites described, when prepared in the presence of organic cations, are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 1000°F for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 1000°F in air. The presence of organic cation in the forming solution may not be absolutely essential to the formation of this type

zeolite; however, the presence of these cations does appear to favor the formation of this special type catalyst by base exchange with ammonium salts followed by calcination in air at about 1000°F for from about 15 minutes to about 24 hours.

5                   Natural zeolites may sometimes be converted to this type zeolite catalyst by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, in combinations. Natural minerals which may be so treated include ferrierite, 10                   brewsterite, stilbite, dachiardite, epistilbite, heulandite, and clinoptilolite. The preferred crystalline zeolites are ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38, with ZSM-5 particularly preferred.

                  In a preferred aspect of this invention, the 15                   zeolites hereof are selected as those having a crystal framework density, in the dry hydrogen form, of not substantially below about 1.6 grams per cubic centimeter. It has been found that zeolites which satisfy all three of these criteria are most desired. Therefore, the preferred 20                   zeolites of this invention are those having a constraint index, as defined above of about 1 to about 12, a silica to alumina mole ratio of at least about 12 and a dried crystal density of not less than about 1.6 grams per cubic centimeter. The dry density for known structures may be 25                   calculated from the number of silicon plus aluminum atoms per 100 cubic Angstroms, as given, e.g., on Page 19 of the article on Zeolite Structure by W. M. Meier. This paper, the entire contents of which are incorporated herein by reference, is included in "Proceedings of the Conference on



Molecular Sieves, London, April 1967", published by the Society of Chemical Industry, London, 1968. When the crystal structure is unknown, the crystal framework density may be determined by classical pykonmeter techniques.

5 For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. It is possible that the unusual sustained activity and stability of this class of zeolites is associated with its high crystal anionic framework  
10 density of not less than about 1.6 grams per cubic centimeter. This high density, of course, must be associated with a relative small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, is important  
15 as the locus of catalytic activity.

Crystal framework densities of some typical zeolites are:

	<u>Zeolite</u>	<u>Void Volume</u>	<u>Framework Density</u>
	Ferrierite	0.28 cc/cc	1.76 g/cc
	Mordenite	.28	1.7
5	ZSM-5 -11	.29	1.79
	ZSM-12	--	1.8
	ZSM-23	--	2.0
	Dachiardite	.32	1.72
	L	.32	1.61
10	Clinoptilolite	.34	1.71
	Laumontite	.34	1.77
	ZSM-4 (Omega)	.38	1.65
	Heulandite	.39	1.69
	P	.41	1.57
15	Offretite	.40	1.55
	Levynite	.40	1.54
	Erionite	.35	1.51
	Gmelinite	.44	1.46
	Chabazite	.47	1.45
20	A	.5	1.3
	Y	.48	1.27

When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of ammonium form to yield the hydrogen form. In addition to the hydrogen form, other forms of the zeolite wherein the original alkali metal has been reduced to less than about 1.5 percent by weight may be used. Thus, the original

alkali metal of the zeolite or introduced hydrogen cations may be replaced by ion exchange with other suitable ions of Groups IB to VIII of the Periodic Table, including, by way of example, nickel, cadmium, copper, zinc, palladium, calcium or rare earth metals.

In practicing the desired method, it may be desirable to incorporate the above-described crystalline aluminosilicate zeolite in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays, which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in a raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the zeolites employed herein may be composited with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia,

silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix may vary widely with the zeolite content ranging from between about 1 to about 99 percent by weight and more usually in the range of about 5 to about 80 percent by weight of the composite.

The degree of zeolite catalyst activity for all acid catalyzed reactions can be measured and compared by means of "alpha value" ( $\alpha$ ). The alpha value reflects the relative activity of the catalyst with respect to a high activity silica-alumina cracking catalyst. To determine the alpha value as such term is used herein, n-hexane conversion is determined at a suitable temperature between about 550°F-1000°F, preferably at 1000°F. Conversion is varied by variation in space velocity such that a conversion level of up to about 60 percent of n-hexane is obtained and converted to a rate constant per unit volume of zeolite and compared with that of silica-alumina catalyst which is normalized to a reference activity of 1000°F. Catalytic activity of the catalysts are expressed as multiple of this standard, i.e. the silica-alumina standard. The silica-alumina reference catalyst contains about 10 weight percent  $Al_2O_3$  and the remainder  $SiO_2$ . This method of determining alpha, modified as described above, is more fully described in the Journal of Catalysis, Vol. VI, pages 278-287, 1966.

One measure of comparison used to relate catalyst activities is "relative activity." Relative activity is the

ratio of the activity of the catalyst after treatment over the initial activity.

Thus relative activity can be expressed as follows:

$$\text{Relative Activity} = \frac{\alpha}{\alpha_0} .$$

5        The relative activity of a catalyst at the point of initial activity is therefore 1 since  $\frac{\alpha}{\alpha_0} = \frac{\alpha_0}{\alpha_0} = 1$ . The relative activity of a catalyst at the point of maximum enhanced activity can be expressed as follows:

$$\text{Relative Activity} = \frac{\alpha}{\alpha_0} = \frac{\alpha_{MA}}{\alpha_0} .$$

10        In order to increase the activity of members of this unique class of zeolites, said zeolites are treated with water, e.g. steam, or water, e.g. steam, produced in-situ. Non-limiting examples of water produced in-situ include alcohol dehydration to produce olefins and steam;  
15        and hydrocarbon or coke combustion in the presence of oxygen to form carbon oxides and steam.

During treatment, the zeolite should be at least partially in the acidic form, e.g. hydrogen form. Suitable zeolitic forms also include those that are at least  
20        partially convertible to the hydrogen form under treatment conditions, e.g. the ammonium form, or alkyl ammonium form.

There exists a narrow range or band of conditions in which zeolite catalyst activity can be enhanced over the initial activity value. Deviations from this band of  
25        conditions can result in either non-enhancement of activity (too mild conditions), or alternatively, catalyst deactivation (too severe conditions). Such conditions include temperature, water partial pressure, treating time, nature of the zeolite, and the nature of the treating gas.

This range of conditions can be clearly demonstrated by a plot of relative activity versus a particular variable, e.g. water partial pressure, treating time, etc., with the other conditions being held constant. Such a plot is given by the drawing in which relative activity is plotted against water partial pressure with temperature and treating time being held constant. With increasing water partial pressure, activity is continuously enhanced above initial relative activity until a point of maximum enhanced relative activity is attained ( $\frac{\alpha_{MA}}{\alpha_0}$ ). Once maximum enhanced relative activity is achieved, the activity begins to decrease with increasing water partial pressure, ultimately back to the same activity as the initial relative activity (same activity as the untreated zeolite, i.e. initial activity). Increasing water partial pressure after this return to initial activity will eventually result in catalyst deactivation (too severe conditions).

Catalyst activation occurs in a limited region of conditions which can be defined as a "zone of enhanced activity". This zone encompasses those conditions which yield activities greater than the initial activity ( $\alpha_0$ ). Thus the zone is that area bounded by the activity of an untreated catalyst-initial activity and the activity of the catalyst when it returns to the initial activity. In terms of relative activities, the zone of enhanced activity is that area bounded by the initial relative activity ( $\frac{\alpha_0}{\alpha_0} = 1$ ) and the return to initial relative activity ( $\frac{\alpha}{\alpha_0} = 1$ ). The zone of enhanced activity embraces all conditions and

combinations thereof yielding activities greater than the initial catalyst activity. One such activity in this zone is the maximum activity. An expression to approximately define this band in relation to two specific variables - treating time and water partial pressure, with temperature held constant is as follows:

$$0.01 (Pt)_T < (Pt) < 10 (Pt)_T$$

$$\text{where } (Pt)_T = 2.6 \times 10^{-9} e^{16000/T}$$

P = Water Partial Pressure, atmospheres

t = Treating Time, hours

T = Temperature, °K

In regard to the condition of zeolite nature, two particular factors can be evaluated. One factor is the specific zeolite employed, such as ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, etc. Another factor is the crystal size of the particular zeolite employed. For the purposes of this disclosure, small crystal size zeolites are those generally of 0.02 to 0.05 microns and large crystal size zeolites are those of generally 0.1 microns and greater.

The use of large crystal size zeolites rather than small crystal size zeolites have the effect of extending the zone of enhanced catalytic activity. Whereas both large and small size zeolites would conform to the above given relationship of  $0.01 (Pt)_T < (Pt) < 10 (Pt)_T$ , for only small size zeolites, the following preferred range is also applicable:

$$0.01 (Pt)_T < (Pt) < 1.0 (Pt)_T.$$

The extent of the zone of enhanced activity can also be modified by adjustments in the controlled conditions of treating time, temperature and water partial pressure. The interdependence of these variables (controlled  
5 conditions) are such that, for example, an increase in water partial pressure, at constant temperature, will lessen the required treating time to attain a certain activity enhancement. Likewise, increasing the temperature, at  
10 constant water partial pressure also lessens the required treating time to attain a specific activity enhancement.

The nature of the treating gas is another influential factor in catalyst activity enhancement. The treating gas in all cases contains either steam or steam  
15 producing compounds and mixtures. However, when ammonia is a constituent of the treating gas, even greater zeolite maximum activities than those attainable by steam alone can be achieved. Also the zone of enhanced activity is extended. The preferred range for ammonia addition is from about 0.01 to about 10 mole ratio ammonia/steam and more  
20 preferably from about 0.1 to about 1.0 mole ratio ammonia/steam.

Zeolites activated in accordance with the present invention are generally useful as catalysts in acid  
25 catalyzed hydrocarbon conversion processes over a range of conversion conditions. Such conditions include a reaction temperature of from about 95° to about 1200°F, preferably from about 390° to about 1000°F, a reaction pressure of from atmospheric to about 10,000 psig, preferably from about atmospheric to about 3,500 psig, and a hydrogen/hydrocarbon.



compound mole ratio of from 0 to about 20, preferably from 0 to about 10. When the conversion is conducted in a flow apparatus, e.g. a down-flow reactor, or under conditions comparable to those existing in a flow apparatus, the weight hourly space velocity (WHSV) should be maintained at between about 0.1 hr<sup>-1</sup> and about 1000 hr<sup>-1</sup>, preferably between about 0.5 hr<sup>-1</sup> and about 10 hr<sup>-1</sup>. When the conversion is conducted in a batch apparatus, e.g. a stirred batch reactor, or under conditions comparable to those existing in a batch apparatus, the contact time should be maintained at between about 0.01 hour and about 48 hours, preferably between about 0.1 hour and about 24 hours.

The subject catalysts have extremely high cracking activity and may be used to convert materials such as gas oils, fuel petroleum crudes, paraffins, olefins and the like from high to low molecular weight substances. The activated catalysts produced by the instant invention may also be used in hydrocracking, alkylation, dealkylation, transalkylation, isomerization, dimerization, oligomerization, polymerization, addition, disproportionation, aromatization, hydration and many other acid catalyzed reactions. A typical alkylation reaction involves the use of aromatics and olefins to synthesize such materials as ethylbenzene, ethyltoluene, or cumene. Another alkylation reaction involves the use of aromatics and paraffins. A typical transalkylation reaction involves reacting benzene and methylnaphthalene to form toluene and naphthalene. Another transalkylation reaction is the conversion of toluene and trimethylbenzene to xylenes. Typical disproportionation

reactions include the conversion of toluene to benzene and xylenes or the conversion of methylnaphthalene to naphthalene and dimethylnaphthalenes. Isomerization reactions may be carried out with diverse feedstocks such as paraffins, olefins or alkyl aromatics, e.g. xylenes.

In particular, when the conversion of hydrocarbon compounds by the present method is olefin polymerization, catalytic conversion conditions should be maintained within certain ranges, including a temperature of from about 95° to about 935°F, preferably from about 390°F to about 810°F, a pressure of from about atmospheric to about 10,000 psig, preferably from about atmospheric to about 2,000 psig, a WHSV (when a flow operation) of from about 0.1 hr<sup>-1</sup> to about 1000 hr<sup>-1</sup>, preferably from about 0.5 hr<sup>-1</sup> to about 100 hr<sup>-1</sup>, and a contact time (when a batch operation) of from about 0.1 hour to about 48 hours, preferably from about 0.5 hour to about 24 hours and a hydrogen/hydrocarbon (i.e. olefin) mole ratio of from about 0 to about 20, preferably from about 0 to about 10.

When the conversion is olefin or paraffin aromatization, catalytic conversion conditions should be maintained within certain ranges, including a temperature of from about 550°F to about 1200°F, preferably from about 650°F to about 1100°F, a pressure of from about atmospheric to about 10,000 psig, preferably from about atmospheric to about 2000 psig, a WHSV (when a flow operation) of from about 0.1 hr<sup>-1</sup> to about 10 hr<sup>-1</sup>, preferably from about 1 hr<sup>-1</sup> to about 5 hr<sup>-1</sup>, a contact time (when a batch operation) of from about 0.1 hour to about 48 hours,

preferably from about 1 hour to about 24 hours and a hydrogen/hydrocarbon, i.e. olefin or paraffin, mole ratio of from about 0 to about 20, preferably from about 0 to about 10.

5                   Further, when the conversion of hydrocarbon compounds by the present process is cracking, catalytic conversion conditions should be maintained within certain ranges, including a temperature of from about 700° to about 1200°F, preferably from about 800° to about 1100°F, a  
10                   pressure of from about atmospheric to about 200 psig, a WHSV (when a flow operation) of from about 0.5 hr<sup>-1</sup> to about 50 hr<sup>-1</sup>, preferably from about 1 hr<sup>-1</sup> to about 10 hr<sup>-1</sup>, and a contact time (when a batch operation) of from about 0.01 hour to about 24 hours, preferably from about 0.1 hour to  
15                   about 10 hours. When the conversion is hydrocracking, catalytic conversion conditions should be maintained within somewhat different ranges, including a temperature of from about 400° to about 1000°F, preferably from about 500° to about 850°F, a pressure of from about 500 psig to about 3500  
20                   psig, a WHSV (when a flow operation) of from about 0.1 hr<sup>-1</sup> to about 10 hr<sup>-1</sup>, preferably from about 0.2 hr<sup>-1</sup> to about 5 hr<sup>-1</sup>, a contact time (when a batch operation) of from about 0.1 hour to about 10 hours, preferably from about 0.2 hour to about 5 hours and a hydrogen/hydrocarbon mole ratio of  
25                   from about 1 to about 20, preferably from about 3 to about 10.

5 When the conversion of hydrocarbon compounds by the instant process is isomerization, conversion conditions include a temperature of between about 450°F and about 1000°F, a pressure of between about 0 and about 500 psig, a WHSV of between about 0.1 and 200 hr<sup>-1</sup>, and a hydrogen to hydrocarbon mole ratio of between about 0.1 and about 10.

10 When the conversion is alkylation or transalkylation by the present process, conversion conditions include a temperature of between about 100°F and about 950°F for alkylation and a temperature of between about 650°F and about 1100°F for transalkylation, a pressure of between about 0 and about 1000 psig for both alkylation and transalkylation, and a WHSV of between about 1 and about 500 for alkylation and of between about 1 and 20 for transalkylation.

15 When the conversion is disproportionation by the instant process, conversion conditions include a temperature of between about 650°F and about 1100°F, a pressure of between about 0 and about 1000 psig, a WHSV of between about 1 and about 20 and a hydrogen to hydrocarbon mole ratio of between about 0 and about 4.

20 The carrying out of the activity enhancement method of this invention can be accomplished concomitant with zeolite manufacture. Alternatively, a conventionally treated catalyst can be utilized in a particular process with enhancement being brought about later, such as in subsequent cycles, or between cycles.

The following examples will serve to illustrate the process of the present invention without unduly limiting same.

EXAMPLE 1

5 A "small crystal size" ZSM-5 with a crystal size of about 0.02 to 0.05 microns was prepared as follows:

A sodium silicate solution was prepared by mixing 16.7 parts water and 28.6 parts sodium silicate (28.7 wt %  $\text{SiO}_2$ , 8.9 wt %  $\text{Na}_2\text{O}$ , 62.4%  $\text{H}_2\text{O}$ ) followed by addition of 0.08  
10 parts Daxad 27 (W.R. Grace Chem. Co.) The solution was cooled to approximately 15°C.

An acid solution was prepared by adding 1 part aluminum sulfate (17.2 wt %  $\text{Al}_2\text{O}_3$ ) to 17.1 parts water, followed by 2.4 parts sulfuric acid (93 wt %  $\text{H}_2\text{SO}_4$ ) and 2.7  
15 parts NaCl.

The silicate solution and the acid solution were mixed in an agitated vessel while 2.0 parts of NaCl and 0.8 parts water were added to form a gel.

An organic solution was prepared by adding 1.9  
20 parts tri-n-propylamine, 1.7 parts n-propyl bromide and 3.2 parts methyl-ethyl ketone.

The organic solution was added to the gel and the mixture was reacted at about 220°F without agitation and held there for 14-15 hours to prereact the organics. At the  
25 end of the prereaction period the agitation was commenced to start the initial crystallization period. After about 75-80 hours the temperature was raised to 320° and held there for about three hours to complete crystallization. The excess

or unreacted organics were flashed off and the remaining contents were cooled and discharged. The zeolite was then washed and dried.

5 The product was identified as ZSM-5 with a sodium level of about 0.01 wt % and having a silica to alumina mole ratio of about 70.

10 After drying, the zeolite was mixed with alpha alumina monohydrate and water to an extrudable consistency and formed into 1/16" extrudates. The extrudates were dried, calcined in flowing N<sub>2</sub> for 3 hours at 1000°F then ion exchanged twice with 1N NH<sub>4</sub>NO<sub>3</sub> solution (5 parts NH<sub>4</sub>NO<sub>3</sub> solution/1 part zeolite) for 1 hour at ambient temperature and dried.

#### EXAMPLE 2

15 A 50 cc sample of ammonium ZSM-5 prepared according to the procedure of Example 1 and containing Al<sub>2</sub>O<sub>3</sub> as a binder material was calcined in an air flow of 1500 cc/min of air to yield a hydrogen form of the zeolite. Aliquot portions of this calcined material were then  
20 calcined for 2-1/2 hours at 1000°F in flowing nitrogen containing various water partial pressures and relative hexane cracking activities were determined at 750°F for purposes of comparison. The results for this example are shown in Table 1 and graphically shown in the drawing.

TABLE 1

Steam Partial Pressure (torr)		Relative Activity for Hexane Cracking at 750°F
5	0	1.0 (starting material)
	5	1.3
	22	2.6
	43	3.5
	55	3.8 (maximum activity)
10	72	3.6
	93	3.0
	149	1.0 (same activity as starting material)
	234	0.61
	760	0.11

As can be seen from Table 1 and the drawing, there is a continuous increase in cracking activity with increasing steam pressure until a maximum activity is attained at 55 torr steam. This maximum activity represents about a four fold increase over the starting material. After this maximum activity is achieved, activities decrease with increasing steam pressure, but still remain higher than the starting material up to 149 torr steam.

EXAMPLE 3

Another sample of small crystal ZSM-5 such as that prepared according to Example 1, was treated at 750°F for 23 hours in one atmosphere steam. The hexane cracking activity of the sample, determined at 1000°F, was increased from an initial activity of  $\alpha = 162$  to a maximum activity of  $\alpha = 200$ .

EXAMPLE 4

A "large crystal size" ZSM-5 with a crystal size of about 1-5 microns was prepared as follows:

A sodium silicate solution was prepared by mixing 16 parts water and 27.7 parts sodium silicate (28.7

wt %  $\text{SiO}_2$ , 8.9 wt %  $\text{Na}_2\text{O}$ , 62.4%  $\text{H}_2\text{O}$ ) followed by addition of 0.08 parts Daxad 27 (W.R. Grace Chem. Co.) The solution was cooled to approximately  $15^\circ\text{C}$ .

5 An acid solution was prepared by adding 1 part aluminum sulfate (17.2 wt %  $\text{Al}_2\text{O}_3$ ) to 16.4 parts water, followed by 2.4 parts sulfuric acid (93 wt %  $\text{H}_2\text{SO}_4$ ) and 1.2 parts  $\text{NaCl}$ .

10 These solutions were mixed in an agitated vessel while 3.9 parts of  $\text{NaCl}$  were added. The gel molar ratios expressed as oxides are the following:

$$\text{SiO}_2/\text{Al}_2\text{O}_3 = 78.4$$

$$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 49.9$$

15 An organic solution was prepared by adding 1.6 parts n-propyl bromide and 3.1 parts methyl-ethyl ketone to 1.9 parts tri-n-propylamine and added to the gel.

The mixture was reacted at  $150\text{-}160^\circ\text{F}$  with severe agitation for 29 hours.

20 The zeolite slurry product was diluted with 4-5 parts water per part slurry and 0.0002 parts of flocculent (Rohm & Haas Primafloc C-7) per part slurry, allowed to settle and supernatant liquid was drawn off. The settled solids were reslurried to the original volume of the preceding step with water and 0.00005 parts of flocculent per part slurry. After settling, the aqueous phase was  
25 decanted. This procedure was repeated until the decant supernatant liquid was  $\text{Cl}^-$  free. The washed zeolite was then filtered, dried and identified as ZSM-5 having a silica/alumina mole ratio of at least 12; i.e., about 70, and a constraint index of between 1 and 12; i.e., about 8.3.



The dried zeolite product was calcined in flowing  $N_2$  for 3 hours at 538°C then ion exchanged twice with 1N  $NH_4NO_3$  solution (5 parts  $NH_4NO_3$  sol'n/1 part zeolite) for 1 hour at ambient temp. and dried at about 120°C.

5

EXAMPLES 5 to 7

10

Large crystal size ZSM-5 prepared according to Example 4 and used in its hydrogen form was treated at three different temperatures, all in one atmosphere steam for various amounts of time. Example 5 was conducted at 750°F; Example 6 was conducted at 800°F and Example 7 was conducted at 1000°F. Relative activities measured at 1000°F in terms of alpha values were evaluated for all the time intervals in all three examples. The results for these examples are given in Table 2.

**TABLE 2**

<u>Example No.</u>	<u>Temperature of</u>	<u>Time, Hours</u>	<u>Relative Activity</u>	<u><math>\frac{\alpha}{\alpha_0}</math></u>
5	750	duration — of catalyst activation 170	1.00	(maximum point)
			2.41	
			1.31	
			0.51	
6	800	0 1.9 4 8 25	1.00	(maximum point)
			1.68	
			2.04	
			2.20	
			2.09	
7	1000	duration — of catalyst activation 3.2 4	1.00	(maximum point)
			2.68	
			1.16	
			1.00	
			0.70	

In comparing the results of Examples 5, 6 and 7 against each other, the effect of temperature can be evaluated. In increasing the temperature, the time required to reach the maximum relative activity is decreased. At 750°F, the maximum relative activity is achieved after 23 hours, while at 800°F, the maximum relative activity is attained after 8 hours. At 1000°F, only 2 hours is required to attain the maximum relative activity. Consequently, when temperature is increased, the duration of catalyst activation is decreased. At 750°F, the duration of catalyst activation is between 70 hours and 170 hours, while at 1000°F, the duration of catalyst activation is only 3.2 hours. The "duration of catalyst activation" is defined as the amount of treating time required for the catalyst activity to return to its initial value (to a value of relative of activity = 1).

#### EXAMPLE 8

ZSM-5 with a crystal size of about 0.1 - 0.5 microns was prepared as follows:

A sodium silicate solution was prepared by mixing 16 parts water and 27.7 parts sodium silicate (28.7 wt %  $\text{SiO}_2$ , 8.9 wt %  $\text{Na}_2\text{O}$ , 62.4%  $\text{H}_2\text{O}$ ). The solution was cooled to approximately 15°C.

An acid solution was prepared by adding 1 part aluminum sulfate (17.2 wt %  $\text{Al}_2\text{O}_3$ ) to 16.4 parts water, followed by 2.4 parts sulfuric acid (93 wt %  $\text{H}_2\text{SO}_4$ ) and 1.2 parts  $\text{NaCl}$ .

These solutions were mixed in an agitated vessel while 3.9 parts of NaCl were added. The gel molar ratios expressed as oxides are the following:

SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 78.4

5 Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 49.9

An organic solution was prepared by adding 1.6 parts n-propyl bromide and 3.1 parts methyl-ethyl ketone to 1.9 parts tri-n-propylamine.

10 After the gel was heated to about 95°C, agitation was reduced and the organic solution was added above the gel. This mixture was held at about 95-110°C for 14 hours, then agitation increased and the temperature was increased to about 150-160°C and held there until crystallization was complete. Unreacted organics were removed by flashing and  
15 the remaining contents cooled.

The zeolite slurry product was diluted with 4-5 parts water per part slurry, allowed to settle and supernatant liquid was drawn off. The settled solids were reslurried to the original volume of the preceding step with  
20 water. After settling, the aqueous phase was decanted. This procedure was repeated until the sodium level of the zeolite was less than 1.0 wt%. The washed zeolite was then filtered, dried and identified as ZSM-5 having a silica/alumina mole ratio of at least 12; i.e., about 70,  
25 and a constraint index of between 1 and 12; i.e., about 8.3.

EXAMPLES 9 and 10

5       The intermediate size zeolite ZSM-5 prepared  
according to the procedure of Example 8 and used in its  
hydrogen form was heated at a rate of 20°C per minute in a  
stream of dry helium. This zeolite had an initial activity  
in terms of alpha value of 211. In Example 9, the HZSM-5 has  
heated to 1400°F and held for 2 hours at that temperature.  
In Example 10, the HZSM-5 was heated to 1800°F and then  
rapidly cooled. After treatments according to Example 9 and  
10       Example 10, the activities of the zeolite in terms of alpha  
value were determined. The results for these examples is  
shown in Table 3.

TABLE 3

<u>Example No.</u>	<u>Final Temperature. of</u>	<u>Time Held at</u> <u>Final Temperature, hrs.</u>	<u>Initial</u> <u>Activity</u> <u><math>\alpha_c</math></u>	<u>Final</u> <u>Activity</u> <u><math>\alpha_c</math></u>
9	1400	2	211	240
10	1800	0	211	300

EXAMPLE 11

HZSM-11 was prepared according to the procedure given in Example 6, Table II of U.S. Patent 4,108,881 and was converted to  $\text{NH}_4\text{ZSM-11}$  by the following method:

5 Three grams of the HZSM-11 was air calcined for 10 hours in a muffle furnace. It was then exchanged twice, at room temperature, with stirring, with 200 ml. of 0.5N  $\text{NH}_4\text{Cl}$  solution for two hours per exchange. It was washed and air dried.

EXAMPLE 12

10 The  $\text{NH}_4\text{ZSM-11}$  prepared according to the general procedure of Example 11 was heated for 10 hours at 1000°F in a closed container, thus providing an atmosphere containing both steam and ammonia. This treatment resulted in a 3.1  
15 fold increase in catalytic activity relative to a sample that was treated in an inert atmosphere.

EXAMPLE 13

Another  $\text{NH}_4\text{ZSM-11}$  sample was prepared according to the following procedure:

20 A sodium silicate solution was prepared by mixing 14.4 parts sodium silicate (28.7 wt %  $\text{SiO}_2$ , 8.9 wt %  $\text{Na}_2\text{O}$ , 62.4 wt %  $\text{H}_2\text{O}$ ) with 8.4 parts water and 0.04 parts Daxad 27 (W.R. Grace Chem. Co.).

25 An acid solution was prepared by mixing 1 part aluminum sulfate (17.2 wt %  $\text{Al}_2\text{O}_3$ ), 1.4 parts sulfuric acid, 0.8 parts sodium chloride and 6.3 parts water.

The silicate solution and acid solution were combined in a mixing nozzle and the resulting gel discharged into an agitated vessel to which 0.4 parts of water had been

added. The gel was thoroughly mixed at ambient temperature and 0.6 parts of sodium chloride was added to the mixture. Finally, a solution containing 1.4 parts of tetrabutylammonium bromide and 2.1 parts water was added to the mixture. The temperature of the gel mixture was raised to 220°F with severe agitation and held for 256 hours until crystallization was complete. The crystallized product was cooled, filtered, washed free of soluble salts and dried. The dried product was analyzed by X-ray diffraction and identified as ZSM-11.

#### EXAMPLE 14

The  $\text{NH}_4\text{ZSM-11}$  prepared according to the general procedure of Example 13 was heated for 10 hours at 1000°F in a closed container. The treatment resulted in a 4.2 fold increase in catalytic activity relative to a sample treated in an inert atmosphere.

#### EXAMPLE 15

Zeolite ZSM-12 was prepared according to the following procedure:

A reaction mixture was prepared by mixing 65 parts of Hi-Sil (a precipitated  $\text{SiO}_2$ ), 6.3 parts NaOH, 1 part  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 40 parts tetraethylammonium bromide and 310 parts  $\text{H}_2\text{O}$ . The mixture was charged to a vessel, thoroughly agitated and heated to about 320°F and held for about 16 hours with agitation. At this point the reaction mixture was cooled and 1.1 parts of  $\text{NaAlO}_2$  and 2.7 parts  $\text{H}_2\text{O}$  were added. The reaction mixture was reheated to 320°F and held for an additional 24 hours at 320°F with agitation to complete crystallization.



The crystallized product was washed and dried and then identified as 90% ZSM-12 by X-ray diffraction with the following chemical analysis:

	<u>% Wt</u>
5            Al <sub>2</sub> O <sub>3</sub>	1.79
SiO <sub>2</sub>	95.1
Na	0.34
N	0.98
C	7.63

10            The washed and dried zeolite was calcined in flowing N<sub>2</sub> for 3 hours at 1000°F then ion exchanged three times with 1N NH<sub>4</sub>NO<sub>3</sub> solution (5 parts NH<sub>4</sub>NO<sub>3</sub> sol'n/1 part zeolite) for 1 hour at ambient temperature and dried at about 250°F.

15            EXAMPLE 16  
A sample of HZSM-12 prepared according to the general procedure of Example 15 was heated in flowing steam of 1 atmosphere pressure at 850°F for various amounts of time. The results for this example are illustrated in Table 4.

20            TABLE 4

<u>Time, hours</u>	<u>Activity</u>
0	138
2	308
5	179
25            10	138

EXAMPLE 17

A sample of HZSM-5 prepared according to the general procedure of Example 4 was steam activated for 10 hours at 1000°F in a closed container. Toluene at a rate of 10 WHSV and 1 atmosphere pressure was passed over both the treated and untreated HZSM-5 catalyst at 900°F in a vertical flow reactor. Toluene was disproportionated to benzene, xylenes and small amounts of trimethyl benzenes. The results of Example 17 are exhibited in Table 5.

TABLE 5

<u>CATALYST</u>	<u>TOLUENE CONVERSION</u>
Untreated Catalyst	8.5%
Steam Treated Catalyst	13.0%

EXAMPLES 18 and 19

In these examples small crystal HZSM-5 with a initial hexane cracking activity of 191 prepared according to the general procedure of Example 1 was utilized. The zeolite in each example was treated with a flowing stream of a particular gas at 1000°F. Results for these examples are given in Table 6.

TABLE 6

<u>Example No.</u>	<u>Nature of Treating Gas</u>	<u>Change in Activity</u>
18	Helium	None
19	Helium Containing 6 Vol. % NH <sub>3</sub>	1.7 Fold Increase

EXAMPLE 20

5       The experimental procedure and catalyst used in  
this example were the same as described in Example 2, except  
that in this example an inert gas stream containing about  
3-14 vol. % ammonia was utilized along with the specified  
partial pressure amounts of steam. After each treatment,  
the sample was heated in a dry nitrogen stream to 1000°F to  
remove adsorbed water and ammonia and the relative activity  
for cracking hexane was determined at 750°F. The results  
10       for Example 20 are given in Table 7.

TABLE 7  
Relative Activity for Hexane Cracking at 750°F

<u>Steam Pressure, (torr)</u>	<u>Relative Activity for Hexane Cracking at 750°F</u>
0	1.0 (starting material)
5	2.5
19	4.6
50	8.6
107	8.8 (maximum activity)
128	7.4
258	4.6
683	1.4

While either steam treatment or ammonia treatment alone produce a catalyst with enhanced activity under mild conditions, the simultaneous presence of steam and ammonia has an unexpected additional synergistic effect above that of the individual gases, as shown in Example 20.

As can be seen by a comparison with Example 2, the synergistic action of both steam and ammonia produce catalysts with even greater activity than by steam treatment alone. In Example 2 where only steam is used, the maximum relative activity is 3.8, whereas in this example where ammonia is added to the steam, the maximum relative activity is 8.8. In addition, the range of treating conditions that give enhanced activities, rather than deactivation is increased. For example, under the conditions of time and temperature of Example 2, the range of beneficial steam pressures is increased from 5 to 149 torr for steam to a range of 5 to about 700 torr steam by the addition of small concentrations of ammonia.

WHAT IS CLAIMED IS:

1. A method for increasing the catalytic activity of an acid zeolite of a certain crystal size having a determinable initial activity and characterized by a silica to alumina mole ratio of at least 12 and a constraint index within the approximate range of 1 to 12, comprising contacting said zeolite with water for a sufficient treating time, temperature and water partial pressure to achieve an activity greater than said initial activity.
2. The method of Claim 1 wherein said zeolite is selected from the group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38.
3. The method of Claim 1 wherein said zeolite is in the hydrogen form.
4. The method of Claim 1 wherein said zeolite is in the ammonium form.
5. The method of Claim 1 wherein said water is liquid water.
6. The method of Claim 1 wherein said water is steam.
7. The method of Claim 1 wherein said water is produced in-situ.
8. The method of Claim 7 wherein said water produced in-situ is from alcohol dehydration.
9. The method of Claim 7 wherein said water produced in-situ is from hydrocarbon combustion in the presence of oxygen.

10. The method of Claim 7 wherein said water produced in-situ is from coke combustion in the presence of oxygen.

11. The method of Claim 1 wherein ammonia is added in amounts ranging from between about 0.01 and about 10 mole ratio ammonia to water.

12. The method of Claim 11 wherein said ammonia is added in amounts ranging from between about 0.1 and about 1.0 mole ratio ammonia to water.

13. The method of Claim 1 wherein a maximum enhanced activity is attained.

14. The method of Claim 1 wherein treating time, temperature and water partial pressure are selected such that the increased catalytic activity is within a zone of enhanced activity, said zone defined as encompassing all those conditions of treating time, temperature and water partial pressure and combinations thereof which yield catalytic activities greater than the initial activity.

15. The method of Claim 1 wherein said sufficient contact time, temperature and water partial pressure is represented by the following relationship of treating time and water pressure at constant temperature:

$$0.01 (Pt)_T < (Pt) < 10 (Pt)_T$$

$$\text{where } (Pt)_T = 2.6 \times 10^{-9} e^{16000/T}$$

P = Water Partial Pressure, atmospheres

t = Treating Time, Hours

T = Temperature, °K



16. The method of Claim 15 wherein said zeolite has a crystal size of 0.02 to 0.05 microns and said relationship of treating time and water pressure at constant temperature is as follows:

5 
$$0.01 (Pt)_T < (Pt) < 1.0 (Pt)_T$$

17. The acid zeolite produced by the methods of Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 or 16.

18. A process for hydrocarbon compound acid catalyzed conversion which comprises contacting a hydrocarbon compound containing feedstock under hydrocarbon conversion conditions with an acid zeolite containing catalyst whose activity has been increased according to the method of Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16.

19. The process of Claim 18 wherein said conversion is conducted in a flow apparatus and said conversion conditions include a temperature of between about 95° and about 1200°F, a pressure of between about atmospheric and about 10,000 psig, a hydrogen/hydrocarbon compound mole ratio of between about 0 and about 20 and a WHSV of between about 0.1 and about 1000 hr<sup>-1</sup>.

20. The process of Claim 18 wherein said conversion is conducted in a batch apparatus and said conversion conditions include a temperature of between about 95°F and about 1200°F, a pressure of between about atmospheric and about 10,000 psig, a hydrogen/hydrocarbon

compound mole ratio of between about 0 and about 20 and a contact time of between about 0.1 and about 48 hours.

21. The process of Claim 18 wherein said conversion is cracking conducted in a flow apparatus and said conversion conditions include a temperature of between about 700° and about 1200°F a pressure of between about atmospheric and about 200 psig and a weight hourly space velocity of between about 0.5 hr<sup>-1</sup> and about 50 hr<sup>-1</sup>.

22. The process of Claim 18 wherein said conversion is cracking conducted in a batch apparatus and said conversion conditions include a temperature of between about 700° and about 1200°F, a pressure of between about atmospheric and about 200 psig and a contact time of between about 0.01 hour to about 24 hours.

23. The process of Claim 18 wherein said conversion is disproportionation and said conversion conditions include a temperature of between about 650°F and about 1100°F, a pressure of between about 0 and about 900 psig, a WHSV of between about 1 and about 20 hr<sup>-1</sup> and a hydrogen to hydrocarbon mole ratio of between about 0 and about 4.

24. The process of Claim 18 wherein said conversion is isomerization and said conversion conditions include a temperature of between about 450°F and about 1000°F, a pressure of between about 0 and about 500 psig, a WHSV of between about 0.1 and 200 hr<sup>-1</sup>, and a hydrogen to hydrocarbon mole ratio of between about 0.1 and about 100.

25. The process of Claim 18 wherein said conversion is alkylation and said conversion conditions include a temperature of between about 100°F and 950°F, a pressure of between about 0 and about 1000 psig, and a WHSV of between about 1 and about 500.

26. The process of Claim 18 wherein said conversion is transalkylation and said conversion conditions include a temperature of between about 650°F and 1100°F, a pressure of between about 0 and about 1000 psig and a WHSV of between about 1 and about 20.

27. The process of Claim 18 wherein said conversion is aromatization conducted in a flow apparatus and said conversion conditions include a temperature of between about 550° and about 1200°F, a pressure of between about atmospheric and about 4,000 psig, a hydrogen/hydrocarbon mole ratio of between about 0 and about 20 and a weight hourly space velocity of between about 0.1 hr<sup>-1</sup> and about 10 hr<sup>-1</sup>.

28. The process of Claim 18 wherein said conversion is aromatization conducted in a batch apparatus and said conversion conditions include a temperature of between about 550° and about 1200°F, a pressure of between about atmospheric and about 4,000 psig, a hydrogen/hydrocarbon mole ratio of between about 0 and about 20 and a contact time of between about 0.1 hour and about 48 hours.

29. The process of Claim 18 wherein said conversion is olefin polymerization conducted in a batch apparatus and said conversion conditions include a temperature of between about 95°F and 935°F, a pressure of between about atmospheric and 10,000 psig, a WHSV of between about 0.1 and 1000 hr<sup>-1</sup> and a hydrogen to hydrocarbon mole ratio of between about 0 and about 20.

30. The process of Claim 18 wherein said conversion is olefin polymerization conducted in a batch apparatus and said conversion conditions include a temperature of between about 95°F and 935°F, a pressure between about atmospheric and 4,000 psig, a contact time of between about 0.1 and about 48 hours and a hydrogen to hydrocarbon mole ratio of between about 0 and about 20.

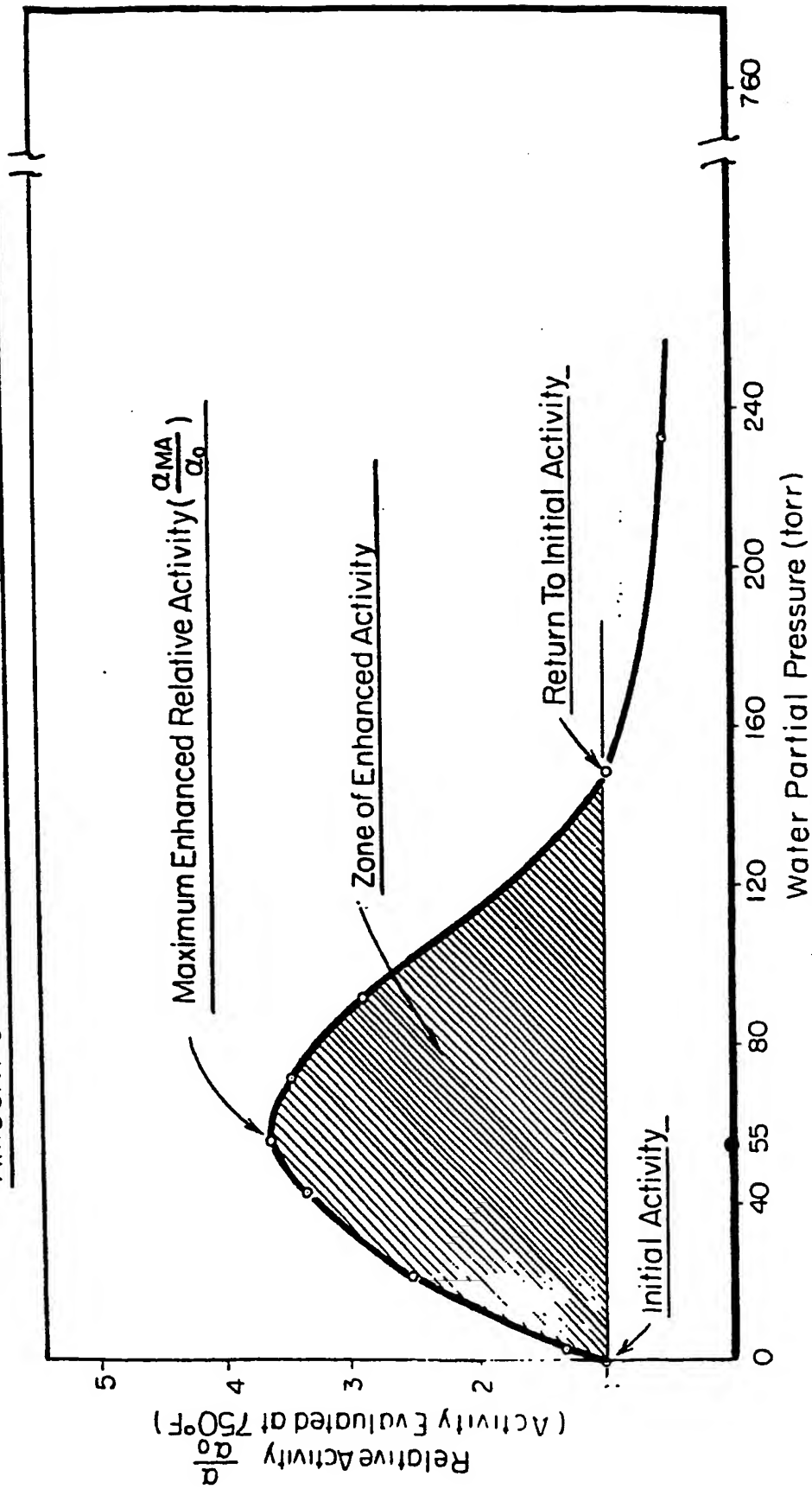
31. The process of Claim 18 wherein said conversion is hydrocracking conducted in a flow apparatus and said conversion conditions include a temperature of between about 400°F and 1000°F, a pressure of between about 500 psig and 3500 psig, a WHSV of between about 0.1 hr<sup>-1</sup> and 10 hr<sup>-1</sup> and a hydrogen/hydrocarbon mole ratio of between about 1 and 20.

32. The process of Claim 18 wherein said conversion is hydrocracking conducted in a batch apparatus and said conversion conditions include a temperature of between about 400°F and 1000°F, a pressure of between about 500 psig and 3500 psig, a contact time of between about 0.1 hour and 10 hours, and a hydrogen/hydrocarbon mole ratio of between about 1 and 20.

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33. The process of Claim 14 wherein said acid zeolite is composited with a matrix material.

DEPENDENCE OF RELATIVE ACTIVITY FOR n-HEXANE CRACKING ON  
AMOUNT OF WATER PRESENT IN CALCINATION OF HZSM-5/Al<sub>2</sub>O<sub>3</sub>





Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 109 060**  
**A1**

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 83111241.2

(51) Int. Cl.<sup>3</sup>: **C 07 C 11/06, C 07 C 4/10,**  
**B 01 J 29/28, B 01 J 29/04**

(22) Date of filing: 10.11.83

(30) Priority: 10.11.82 IT 2415382  
24.12.82 IT 2497982  
14.03.83 IT 2005383  
03.05.83 IT 2089883

(43) Date of publication of application: 23.05.84  
Bulletin 84/21

(84) Designated Contracting States: DE FR GB IT

(71) Applicant: MONTEDIPE S.p.A., 31, Foro Buonaparte,  
Milan (IT)

(72) Inventor: Colombo, Fausto, 60/A, Via Verdi, Merate  
(Como) (IT)  
Inventor: Alberti, de Giordano, 4, Largo Brianconi,  
Besenato (Varese) (IT)  
Inventor: Padovan, Mario, 1, Via Villa Mirabello, Milano  
(IT)  
Inventor: Papparatto, Giuseppe, 8, Via Buoizzi, Cinisello  
Balsamo (Milano) (IT)  
Inventor: Contassa, Socrata, 35, Via Repubblica, Senago  
(Milano) (IT)

(74) Representative: Barz, Peter, Dr. et al, Patentanwälte Dr.  
V. Schmied-Kowarzki Dipl.-Ing. G. Dannenberg Dr. P.  
Weinhold Dr. D. Gudel Dipl.-Ing. S. Schubert Dr. P. Barz  
Siegfriedstrasse 8, D-8000 München 40 (DE)

(54) Process for the conversion of olefins having from 4 to 12 carbon atoms to propylene.

(57) A process for the conversion of olefins having from 4 to 12 carbon atoms into propylene, characterized in that said olefins are brought into contact with a zeolitic compound (optionally in admixture with a binder), selected from silicalites, borasilites, chromosilicates and those zeolites ZSM5 and ZSM11 in which  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (by moles) is  $> 350$ , at a space velocity of from 5 to 200  $\text{kg/h}$  of olefins per  $\text{kg}$  of pure zeolitic compound (binder excluded) and at a temperature of from 400 to 600°C, said zeolitic compound being used as such or in a modified form.

EP 0 109 060 A1

PROCESS FOR THE CONVERSION OF OLEFINS HAVING FROM 4 TO 12  
CARBON ATOMS TO PROPYLENE

The invention concerns a process for the conversion  
5 of olefins having from 4 to 12 carbon atoms into propylene.

Nowadays huge amounts of olefine cuts, from  $C_4$  to  
 $C_{12}$ , linear or branched, are available throughout the  
world and they are widely employed for different purposes,  
such as described for instance in Italian patent publi-  
10 cations 24152 A/82, 24550 A/82 and 19292 A/83. Sometimes,  
however, because of contingent reasons, even outside the  
chemical field, like for instance transportation difficul-  
ties, it would be better to have still further possibilities  
of use. A promising use of said olefins would be their  
15 conversion into propylene and/or ethylene.

However, endurance tests have shown that the excellent  
initial behavior of some catalysts, like for instance ZSM5  
and ZSM11, disappears after some time; after a few weeks  
conversion and selectivity drop to poor levels.

20 An object of the invention is to provide a process for  
catalytically converting olefin cuts  $C_4$  -  $C_{12}$  with high  
propylene (and optionally also ethylene) yields and with  
a long life time of the catalyst before substitution or  
regeneration.

25 In its most general form, the invention concerns a  
process for the conversion of olefins having from 4 to 12  
carbon atoms into propylene which is characterized in that  
said olefins are brought into contact with a zeolitic com-  
pound (optionally in admixture with a binder) selected  
30 from silicalites, boralites, chromosilicates and those  
zeolites ZSM5 and ZSM11 in which  $SiO_2/Al_2O_3$  (by moles) is  
 $\geq 350$ , at a space velocity of from 5 to 200 kg/h of olefins  
per kg of pure zeolitic compound, binder excluded, and at  
a temperature of from 400 to 600°C, said zeolitic compound  
35 being used as such or in a modified form.



The behavior of silicalites depends on the conversion pressure; for instance, if the silicalite is silicalite-1 and if the pressure is substantially atmospheric, the space velocity must be lower than  $50 \text{ h}^{-1}$ ; if said compound is silicalite-1 and if the pressure is from 1.5 to 7.5 absolute atmospheres the space velocity must be in general above  $50 \text{ h}^{-1}$ .

Best results are obtained when said catalytic silicalite-1 is activated in the conversion reaction of the olefins into propylene, under said operative conditions. This initial (activating) run takes at least 8 and preferably 12 hours; the silicalite-1 is used as such or in a modified form and the modifying element is selected from Cr, Mg, Ca, Sr and Ba.

The modifying element can be incorporated into the catalyst by means of ion exchange or by any other method, for instance impregnation or co-precipitation during the synthesis of the zeolitic compound.

According to a particularly advantageous way for the preparation of a non-modified silicalite, the raw product coming from the zeolite synthesis is dried, for instance at  $120^\circ\text{C}$ , calcined (e.g. at  $540^\circ\text{C}$  for some hours), in order to remove all the residual organic templating agent, and then exchanged with an aqueous solution of  $\text{HCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$  or an equivalent  $\text{H}^+$  or  $\text{NH}_4^+$  source. When an ammonium compound is used, it is necessary to heat, e.g. at  $400^\circ\text{C}$ , in order to obtain the acid form of the silicate. A survey of techniques alternative to ion exchange is given e.g. in U.S. patents 3,140,249; 3,140,251; 3,140,253 and in European patent publications 30796, 36707, 37168, 40463, 68754.

The zeolitic material, after calcination and conversion into the acid form, shows a long endurance and a very high catalytic activity. These zeolitic compounds can be used as catalysts (as such or in a modified form) optionally in admixture with suitable amounts of binders, for instance  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ . A list of other binders can be found

e.g. in European patent publication 36707. The regeneration can be carried out in air for some hours, at 400-600°C. A  
5 steam regeneration is described in European patent publication 36704 and according to a further and very successful method, the catalyst can be regenerated by a hydrogen treatment.

As to the initial activation of the catalyst, some  
10 methods are described in European patent publications 34444 and 35830; in general it is advisable to activate the catalyst for some hours in air, at 450-750°C (preferably 540-700°C). Furthermore the conversion itself (of olefins to propylene) has an activating effect on the zeolitic  
15 catalyst. In other words, catalyst and reaction affect each other in a mutual, reciprocal and beneficial activating reaction.

Any process for the conversion of more or less heavy olefinic cuts into propylene will be indicated hereafter,  
20 as a "post-pyrolysis" process. When the feed of a post-pyrolysis process is a mixture of olefins having 4 C atoms, there is a considerable problem to be solved, because the C<sub>4</sub> cuts always contain substantial amounts of paraffins, in general, also having 4 C atoms, which paraffins pass  
25 (at 400-600°C) the zeolitic bed without taking part in any reaction. Furthermore a small amount of C<sub>4</sub><sup>-</sup> paraffins is produced by the post-pyrolysis process itself. The conversion to C<sub>3</sub>H<sub>6</sub> could be enhanced by a recycle of the non-reacted C<sub>4</sub><sup>-</sup> olefins or of the C<sub>4</sub><sup>-</sup> olefins formed during the  
30 reaction. In such a case, however, an increasing accumulation of n-butane and of isobutane would take place. This drawback could be avoided by a separation of paraffins from olefins before feeding the reactor but such a separation is rather difficult. Butenes and isobutane can-  
35 not be isolated by a simple distillation and it is usually necessary to carry out an extractive distillation (a complicated technique), which is particularly burdensome for the C<sub>4</sub><sup>-</sup> cuts coming from catalytic cracking, where butane and isobutane may account for even 50% of the whole. The problem, however, can be solved in a surprisingly easy way

by the process according to the invention, when employing an integrated oligomerization step. In other words, a particular embodiment of the invention (the feed being a paraffin-olefin mixture) comprises the following steps (reference is made also to figure 2):

- a) preliminary oligomerization of a ( $C_4^- + C_4^+$ ) mixture at a temperature of from 320 to 380°C using a catalyst bed of zeolitic nature (see e.g. U.S. patent 4,150,062) to obtain a mixture of olefins having from 5 to 8 C atoms, with the  $C_4^+$  paraffins remaining unconverted;
- b) cooling and condensation of the oligomerization effluent in order to separate the  $C_4^+$  paraffins as a gaseous phase, and conversion of the remaining ( $C_5^- - C_8^-$ ) mixture to propylene under typical "post-pyrolysis" operative conditions;
- c) cooling of the effluent from the reactor for the conversion to propylene and compression of said effluent, preferably at 13-16 absolute Kg/cm<sup>2</sup>, whereby the hydrocarbons having 4 or more C atoms are condensed and the hydrocarbons having less than 4 C atoms are separated as a gaseous phase.

These hydrocarbons ( $< C_4$ ) can be advantageously recycled to a conventional battery of distillation columns for thermal or catalytic cracking, in order to recover all the propylene contained therein. The small and possible amounts of aromatics (BTX) can be easily separated from the other  $C_4$  hydrocarbons and recycled together with the final ( $C_4^- - C_8^-$ ) mixture, containing small amounts of butanes produced during the conversion reaction described under item (b) above.

In order to carry out the oligomerization,  $C_4$  olefins, containing  $C_4$  paraffins in any proportion, are initially brought into contact with a catalyst of zeolitic nature, for instance ZSM5 or ZSM11, in an acid or in a modified form, at 250-400°C (preferably 320-380°C) and at space

velocities from 2 to 10 (preferably 4 - 8) kg/h of reactants per kg of pure zeolite (binder excluded). In other words, the olefins of the ( $C_4^- + C_4^+$ ) mixture are converted almost totally into a ( $C_5^- - C_8^-$ ) olefinic mixture, while butane and isobutane do not react. The separation of the butanes can thus be carried out very easily by simple cooling with water at room temperature. The olefinic ( $C_5^- - C_8^-$ ) mixture liquifies while the butanes are separated as a gaseous phase, said ( $C_5^- - C_8^-$ ) mixtures being optimal raw-materials for the production of propylene.

Depending on the operative conditions of the synthesis of the silicalite, as e.g. the dilution of the starting solutions, the resulting crystallites may have a widely variable size. The crystallites to be employed in the process according to the invention should have, in general, rather small sizes, such small sizes being obtainable, for instance, following the teachings of U.S. patent 3,926,782. The following examples are given merely for illustration purposes and do not in any way limit the scope of the invention.

#### OPERATIVE CONDITIONS COMMON TO ALL EXAMPLES

As to the method of preparation of the catalysts see:

- for silicalite-1: U.S. patent 4,061,724;
- for boralite: Taramasso et al.: "Molecular Sieve Borosilicates", Proc. 5th Int. Conf. on Zeolites, Naples 1980, pages 40-48 (Heyden and Son Ltd. London 1980); the boralite used in the examples has a ratio  $SiO_2 : B_2O_3$  of 7 (by moles); a more recent method for obtaining boro-silicates is described in European patent publication 77946 .
- for chromosilicates: Italian patent publication 22568 A/82, in the name of the Applicant; the chromosilicate used in the examples has a ratio  $SiO_2 : Cr_2O_3$  of 38 (by moles).

As to zeolites ZSM5 showing a very high  $SiO_2 : Al_2O_3$  ratio, not exemplified, see Italian patent publication 21699 A/83, in the name of the Applicant. In the absence of different indications, all the catalysts were activated 2 hours at 540°C before being used.

EXAMPLES 1-6

3 g of zeolitic catalyst, in admixture with 0.9 g of  
5  $\text{SiO}_2$  (as a binder), were loaded into a microreactor which  
was continuously fed, at a pressure slightly above atmo-  
spheric pressure with a 50/50 mixture of butene-2-trans  
and butene-2-cis. Operative conditions and results are  
given in Table 1.

10 EXAMPLE 7

Example 4 was repeated using a silicalite-1 impregnated  
with a chromium salt, thus obtaining slightly better re-  
sults.

15 EXAMPLES 8-15

0.5 g of zeolitic catalyst, in admixture with 0.21 g  
of  $\text{Al}_2\text{O}_3$  (as a binder), were loaded into a microreactor  
which was continuously fed, at a pressure slightly above  
the atmospheric pressure with a 70/100 mixture of n-pen-  
tene and of helium (by moles). Detailed operative con-  
20 ditions and results are given in Table 2. When modified  
zeolitic catalysts were used, the modifying element was  
added by means of impregnation.

25 EXAMPLES 16-23

Examples 8 and 9 were repeated replacing pentene with  
n-hexene (ex. 16 and 17), with 2-methyl-pentene-1 (ex. 18,  
19 and 20) and with n-octene-1 (ex. 21, 22 and 23), re-  
spectively, the parameters being slightly modified as in-  
dicated in Table 3, which shows also the very good results.

30 EXAMPLES 24-29

2.12 g of zeolitic catalyst were loaded into a micro-  
reactor which was continuously fed with 7.5 kg/h of iso-  
butene per kg of zeolitic catalyst at  $550^\circ\text{C}$  and at a  
pressure slightly above atmospheric pressure. Data and  
35 results are given in Table 4.

EXAMPLES 30 AND 31

Examples 24 and 25 were repeated raising the pressure  
to 5 absolute atmospheres and the space velocity (WHSV)  
from  $7.5$  to  $45 \text{ h}^{-1}$ , thus obtaining analogous results.

EXAMPLES 32-35

3 g of silicalite-1, without binder, were loaded into a microreactor which was continuously fed with 60kg/h of the olefins of example 1 per kg of silicalite, at high pressures (6 absolute atmospheres for example 32 and 33 and 8 abs. atm. for ex. 34 and 35). The detailed operative conditions and the results are given in Table 5. The results show clearly that a slight increase in pressure, corresponding approximately to the pressure of the olefins in the industrial manufacturing plants, allows the same conversions and selectivities, but at a much higher velocity. In other words, it is surprising and was quite unexpected that a suitable increase of the pressure increases very much the productivity of the silicate and therefore the output of the industrial plants.

EXAMPLE 36

50 parts by weight of silicalite-1 were admixed with 50 parts of  $Al_2O_3$  (binder) and the mixture was loaded into a microreactor which was continuously fed at atmospheric pressure, with a 50/50 mixture of butene-2-trans and butene-2-cis, at 550°C and at a space velocity of 20 kg/h of olefins per kg of silicalite (binder excluded). The run was very long (120 h) and the results, hour by hour, were continuously monitored and plotted in figure 1. It is worthwhile to note that the initial decrease of conversion is reversed after a few hours; thus the conversion of the olefins itself is likely to be a stimulating activation for the catalyst. In other words, catalyst and reaction effect each other by a mutual and beneficial activating action.

EXAMPLE 37

Example 36 was repeated by using a mixture 65% b.w. silicate-1 + 35% b.w.  $Al_2O_3$  and by raising the space velocity to 67  $h^{-1}$ . In this case, the conversion initially decreased and then the phenomenon was reversed.

TABLE 1

EXAMPLE	1	2	3	4	5	6
Operative conditions:						
Catalyst	Boralite	see Ex. 1	Silicalite-1	See Ex. 3	Chromosilicate	See Ex. 5
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (moles)	(b)	"	$\infty$	"	(d)	"
Amount of catalyst	3 grams (c)	"	see Ex. 1	"	see Ex. 1	"
Temp. ( $^{\circ}\text{C}$ )	500	"	"	"	"	"
Space velocity (a)	6	"	"	"	"	"
Data survey after:	1 h	5 h	1 h	7 h	1 h	6 h
Results (%w.w.)						
Conversion	45.95	29.01	61.95	77.06	29.75	12.25
Selectivity to iso- $\text{C}_4^-$	29.79	40.40	15.26	12.47	34.07	40.46
Selectivity to $\text{C}_3^-$	28.36	24.90	44.79	10.39	29.73	23.65
Yield (iso $\text{C}_4^- + \text{C}_3^-$ )	26.72	18.94	49.23	45.13	19.88	7.85
Sel. to compounds $\text{C}_4^-$	38.76	31.73	28.15	31.75	32.29	30.82
Sel. to saturated compounds $\leq \text{C}_4^-$	2.51	2.55	6.85	5.44	3.46	4.77
Selectivity to $\text{C}_2^-$	0.57	0.43	4.95	2.95	0.45	0.31

(a) WHSV (Weight Hourly Space Velocity) namely Kg/h of olefine per Kg. of pure catalyst (binder excluded);

(b)  $\text{SiO}_2:\text{B}_2\text{O}_3 = 7$  (by moles);(c) + 0.9 g of  $\text{SiO}_2$  as binder;(d)  $\text{SiO}_2:\text{Cr}_2\text{O}_3 = 38$  (by moles)

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TABLE 2

EXAMPLE	8	9	10	11	12	13	14	15
Operative Conditions:								
Catalyst	Silicalite-1	See Ex. 1	Boralite	See Ex. 10	Chromosilicate	See Ex. 12	Cr-Silicalite	See Ex. 14
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	∞	"	(d)	"	(K)	"	∞	"
Amount of catalyst	(c)	"	See Ex. 8	"	See Ex. 8	"	See Ex. 8	"
Temp. (°C)	550	"	"	"	"	"	"	"
Space velocity (a)	7.14	"	"	"	"	"	"	"
Data survey after:	1 h	6 h	1 h	6 h	1 h	6 h	1 h	6 h
Results (x b.w.)								
Conversion	64.26	57.00	42.81	19.52	16.80	10.04	69.22	60.92
Selectivity to C <sub>2</sub> <sup>-</sup>	19.44	19.80	23.43	27.97	21.25	17.92	20.51	19.63
Selectivity to C <sub>3</sub> <sup>-</sup>	33.19	39.42	39.27	38.93	32.50	29.52	34.25	39.71
yield (C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> )	35.93	33.76	26.84	13.06	9.03	4.77	37.90	36.15
Sel. to saturated compounds < C <sub>4</sub>	0.96	0.70	0.46	0.31	0.65	0.79	0.91	0.76
Sel. to C <sub>4</sub> <sup>+</sup>	29.27	29.42	27.61	24.70	26.90	30.38	29.31	28.37
Sel. to C <sub>4</sub> <sup>+</sup>	1.36	0.84	0.66	0.25	0.29	0.29	1.21	1.88
Sel. to BTX (b)	6.65	5.96	3.59	1.79	7.97	4.58	7.79	6.06
Sel. to others	3.06	3.82	4.95	5.79	10.83	7.27	6.02	3.69

(a) See ex. 1; (b) BTX = benzene + toluene + xylenes; (c) 0.5 g of pure zeolite + 0.21 g of Al<sub>2</sub>O<sub>3</sub> (binder); (d) SiO<sub>2</sub>/B<sub>2</sub>O<sub>3</sub> = 7 (by moles);

(K) SiO<sub>2</sub> : Cr<sub>2</sub>O<sub>3</sub> = 38 (by moles).

(\*) Silicalite-1 containing 0.1% b.w. Cr, added by means of impregnation.



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TABLE 3

EXAMPLE	16	17	18	19	20	21	22	23
Operative Conditions:	(*)	(*)	(**)	(**)	(**)	(***)	(***)	(***)
Catalyst	Silicalite-1	See Ex. 16	See Ex. 16	See Ex. 18	See Ex. 18	See Ex. 16	See Ex. 21	See Ex. 21
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	∞	"	"	"	"	"	"	"
Amount of catalyst	See Ex. 8	"	"	"	"	"	"	"
Temp. (°C)	550	"	"	"	"	"	"	600
Space velocity (a)	7.14	"	"	"	"	"	"	7.14
Data survey after:	1 h	6 h	1 h	6 h	7 h	1 h	6 h	7 h
Results (X b.w.)								
Conversion	98.01	96.83	97.79	97.36	89.9	100	97.47	95.50
Selectivity to C <sub>2</sub> <sup>-</sup>	10.38	9.12	10.55	9.29	7.48	9.16	7.60	16.64
Selectivity to C <sub>3</sub> <sup>-</sup>	51.14	52.90	53.03	53.79	55.35	31.64	31.13	27.56
Yield (C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> )	60.28	60.05	52.17	61.41	56.48	40.80	37.75	42.21
Sel. to saturated compounds < C <sub>4</sub>								
Sel. to C <sub>4</sub> <sup>+</sup>	0.78	0.65	0.60	0.41	0.20	0.62	0.44	0.34
Sel. to C <sub>4</sub> <sup>+</sup>	17.55	14.80	16.78	13.65	11.92	26.96	28.21	24.37
Sel. to C <sub>4</sub> <sup>+</sup>	0.41	0.23	0.30	0.13	0.06	1.06	0.55	0.30
Sel. to BTX (b)	14.64	17.55	13.82	16.54	20.67	24.14	27.08	21.97
Sel. to C <sub>5</sub>	2.81	2.22	1.89	2.76	0.99	2.66	2.05	5.64
Sel. to others	2.20	2.51	2.97	3.40	3.26	3.74	2.77	3.14

(a) See ex. 1 (b) BTX = benzene + toluene + xylenes ; (\*) Feed = n-hexene-1; (\*\*) Feed = 2-methyl-pentene-1; (\*\*\*) Feed = n-octene-1

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TABLE 4

EXAMPLE	24	25	26	27	28	29
Operative conditions:						
Catalyst	Silicalite-1	See Ex. 24	Boralite (a)	See Ex. 26	Chromosilicate (b)	See Ex. 28
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	∞	"	See Ex. 24	"	See Ex. 24	"
Amount of catalyst	2.12 g	"	550	"	550	"
Temp. (°C)	550	"	7.5	"	7.5	"
Space velocity (h <sup>-1</sup> )	7.5	"	1 h	"	1 h	"
Data survey after:	1 h	6 h	1 h	6 h	1 h	6 h
Results (% h.v.)						
Conversion	81.8	77.3	77.4	62.4	44.5	18.1
Selectivity to C <sub>5</sub> <sup>-</sup>	44.8	40.8	39.1	24.8	16.5	12.4
Yield (C <sub>3</sub> <sup>-</sup> )	36.5	31.5	30.3	15.8	7.4	2.2
Sel. to C <sub>2</sub>	4.2	2.6	3.4	1.2	0.8	0.5
Sel. to saturated compounds < C <sub>4</sub>	9.5	5.6	5.7	2.9	5.1	3.9
Sel to compounds > C <sub>5</sub>	6.4	7.0	7.8	5.4	13.7	8.1
Sel to linear butenes	35.1	44.0	44.0	65.7	63.9	75.1

(a) SiO<sub>2</sub> : B<sub>2</sub>O<sub>3</sub> = 7 (by moles); (b) SiO<sub>2</sub> : Cr<sub>2</sub>O<sub>3</sub> = 38 (by moles).

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TABLE 5

EXAMPLE	32	33	34	35
Operative conditions:	(*)	(*)	(**)	(**)
Catalyst	Silicalite-1	See Ex. 32	See Ex. 32	See Ex. 34
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	8	"	"	"
Amount of catalyst	3 g	"	"	"
Temp. (°C)	570	"	580	"
Space velocity (h <sup>-1</sup> )	60	"	60	"
Data survey after:	1 h	8 h	1 h	8 h
Results (% b.w.)				
Conversion	82.24	73.80	79.31	67.32
Selectivity to C <sub>3</sub>	31.98	39.89	39.66	26.00
Yield (C <sub>3</sub> )	26.30	29.44	31.45	17.50
Sel. to C <sub>2</sub>	3.88	3.19	4.21	3.20
Sel. to saturated compounds <C <sub>4</sub>	13.76	10.62	14.14	8.40
Sel. to compounds >C <sub>5</sub>	36.02	25.72	27.80	45.60
Sel. to isobutene	14.76	20.58	14.19	16.50

(\*) Pressure = 6 absolute atmospheres;

(\*\*) Pressure = 9 absolute atmospheres.

CLAIMS

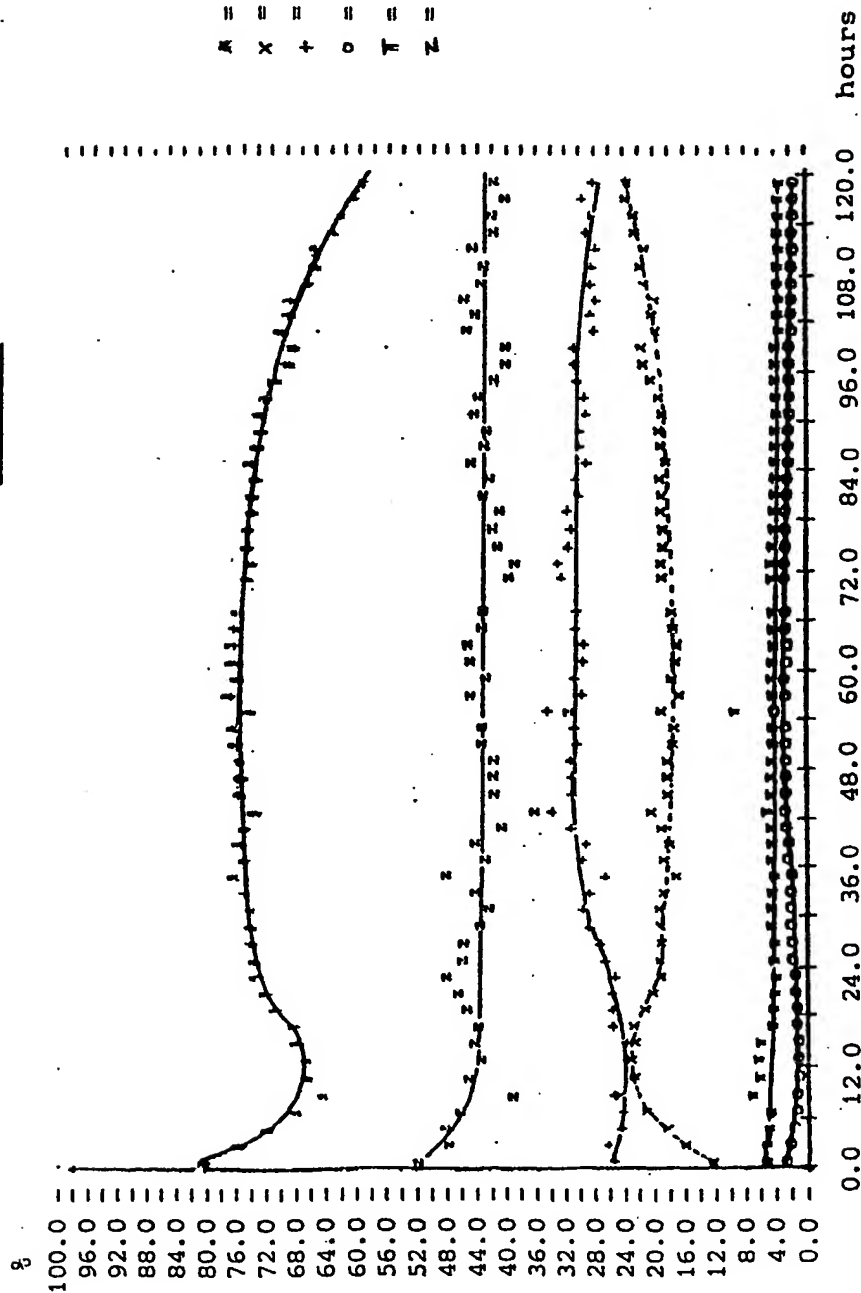
- 5 1. A process for the conversion of olefins having from 4 to 12 carbon atoms to propylene, characterized in that said olefins are brought into contact with a zeolitic compound (optionally in admixture with a binder), selected from silicalites, boralites, chromosilicates and those  
10 zeolites ZSM5 and ZSM11 in which  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (by moles) is  $\geq 350$ , at a space velocity of from 5 to 200 kg/h of olefins per kg of pure zeolitic compound (binder excluded) and at a temperature of from 400 to 600°C, said zeolitic compound being used as such or in a modified  
15 form.
2. The process of claim 1, wherein said compound is silicalite-1, the pressure is substantially atmospheric and the space velocity is from 5 to 50  $\text{h}^{-1}$ .
- 20 3. The process of claim 1, wherein said compound is silicalite-1, the pressure is from 1.5 to 7.5 absolute atmospheres and the space velocity is from 50 to 200  $\text{h}^{-1}$ .
- 25 4. The process of any of claims 1-3, wherein said compound is silicalite-1 which is activated in the conversion reaction of said olefins to propylene, under the operative conditions of claim 1, the initial (activating) run being carried out at least 8 and preferably 12 hours.
- 30 5. The process of any of claims 1-4, wherein said olefins are selected from isobutene and linear butenes and wherein said binder is  $\text{SiO}_2$ .
- 35 6. The process of any of claims 1-4, wherein said olefins contain from 5 to 8 carbon atoms and wherein said binder is  $\text{Al}_2\text{O}_3$ .

7. The process of any of claims 1-6, wherein said compound is silicalite-1 in a non-modified form.
- 5 8. The process of any of claims 1-6, wherein said compound is silicalite-1 in a modified form, the modifying element being Cr, Mg, Ca, Sr or Ba.
- 10 9. A process for the conversion of olefins having 4 carbon atoms into propylene, characterized in that said olefins are brought into contact with a zeolitic compound (optionally in admixture with a binder) selected from silicalites and those zeolites ZSM5 and ZSM11 in which  
15  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (by moles) is  $\geq 350$ , at a pressure of from 1.5 to 7.5 atmospheres, a space velocity of from 50 to 200 kg/h of olefins per kg of pure zeolitic compound (binder excluded) and a temperature of from 400 to 600°C, said compound being used as such or in a form modified  
20 by an element selected from Cr, Mg, Ca, Sr and Ba.
10. A process for the conversion of olefins having from 5 to 8 carbon atoms into propylene, characterized in that said olefins are brought into contact with a zeolitic  
25 compound (optionally in admixture with a binder) selected from silicalites and those zeolites ZSM5 and ZSM11 in which  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (by moles) is  $\geq 350$ , at a pressure of from 1.5 to 7.5 atmospheres, a space velocity of from 50 to 200 kg/h of olefins per kg of pure zeolitic compound (binder excluded) and a temperature of from 400  
30 to 600°C, said compound being used as such or in a form modified by an element selected from Cr, Mg, Ca, Sr and Ba.
- 35 11. The process of claims 9 or 10 wherein said compound is silicalite-1 which is activated in the conversion reaction of said olefins to propylene, under said operative conditions, the initial (activating) run being carried out at least 8 and preferably 12 hours.

12. A process for the conversion into propylene of mixtures  
of olefins having 4 C atoms, said mixtures containing  
also  $C_4^+$  paraffins. that cannot be easily separated from  
olefins, which process comprises the following steps:

- a) preliminary oligomerization of a  $(C_4^- + C_4^+)$  mixture  
at a temperature of from 320 to 380°C using a catalyst  
bed of zeolitic nature to obtain a mixture of olefins  
having from 5 to 8 C atoms, with the  $C_4^+$  paraffins  
remaining unconverted;
- b) cooling and condensation of the oligomerization  
effluent in order to separate the  $C_4^+$  paraffins as a  
gaseous phase, and conversion of the remaining  
 $(C_5^- - C_8^-)$  mixture to propylene under the typical  
"post-pyrolysis" reaction conditions of claim 1;
- c) cooling the effluent from the reactor for the con-  
version to propylene and compression of said effluent,  
preferably at 13-16 absolute  $kg/cm^2$ , whereby the  
hydrocarbons having 4 or more C atoms are condensed  
and the hydrocarbons having less than 4 C atoms  
are separated as a gaseous phase.

FIGURE 1



1/2

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2/2

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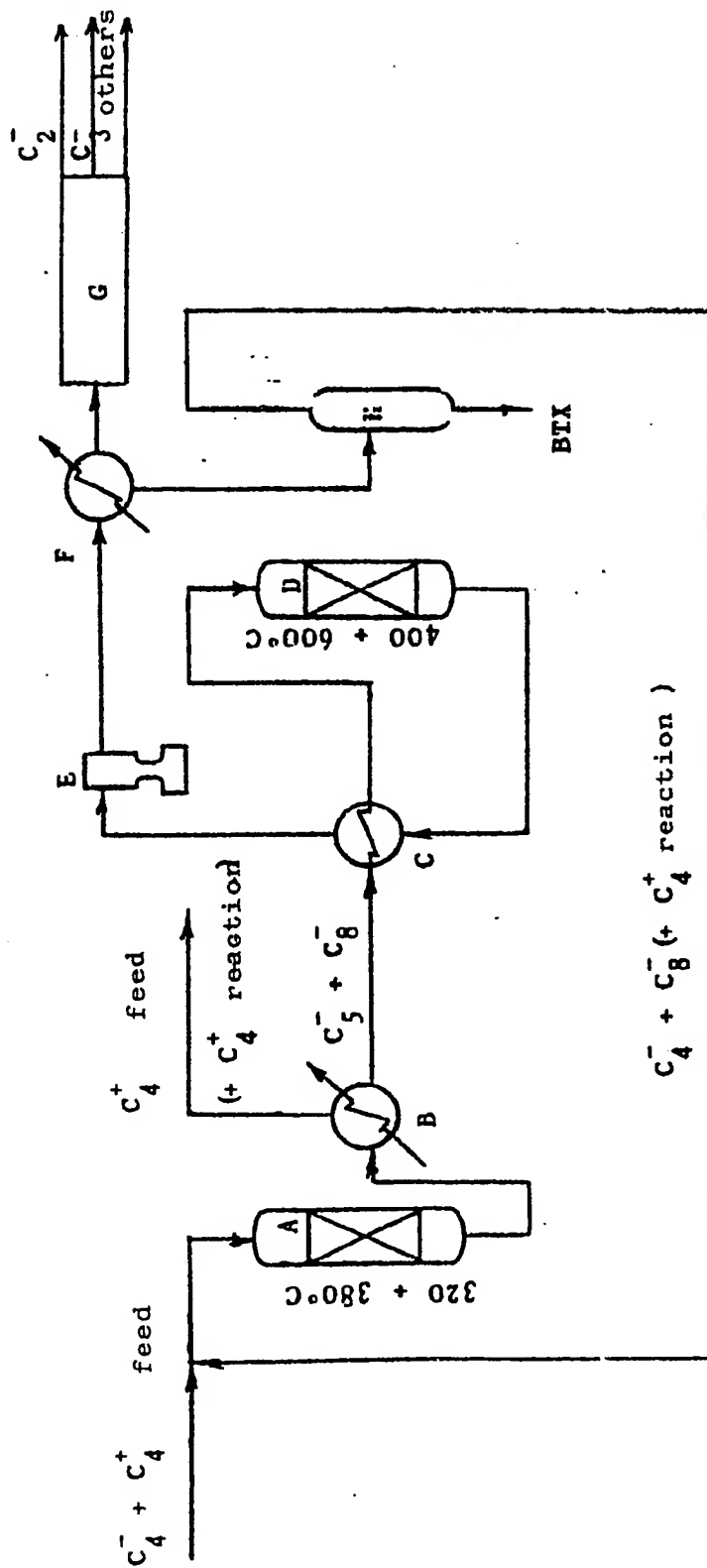


FIGURE 2





European Patent  
Office

# EUROPEAN SEARCH REPORT

0109060  
Application number

EP 83 11 1241

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 8)
1 A	EP-A-O 037 671 (MOBIL OIL CORP.) * Page 11, paragraph 2; claims *	1, 9, 10	C 07 C 11/06 C 07 C 4/10 B 01 J 29/28 B 01 J 29/04
1 A,D	US-A-4 150 062 (GARWOOD et al.) * Examples 5-6; claims * -----	12	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 8)
			C 07 C 11/00 C 07 C 4/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30-01-1984	Examiner VAN GEYT J.J.A.

### CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone  
Y : particularly relevant if combined with another document of the same category  
A : technological background  
O : non-written disclosure  
P : intermediate document

T : theory or principle underlying the invention  
E : earlier patent document, but published on, or after the filing date  
D : document cited in the application  
L : document cited for other reasons

& : member of the same patent family, corresponding document

Serial No. 10/719,267  
31223.00020  
(F-756CON)

### **Related Proceedings Appendix**

Copies of the Decisions on Appeal in the following applications are attached.

Application Serial No. 09/594,059, Abandoned

Application Serial No. 09/206,210, now Patent No. 6,713,658

Application Serial No. 09/205,559, Abandoned

Application Serial No. 09/206,207, now Patent No. 6,645,175

Application Serial No. 09/206,208, now Patent No. 6,646,176

Application Serial No. 09/206,218, now Patent No. 6,951,968

Application Serial No. 09/206,216, now Patent No. 7,087,155

Application Serial No. 09/596,356, Abandoned

F-756  
31223/80538  
Walg.

The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

RECEIVED

Request for Reconsideration  
Due: 11/24/03

Paper No. 19

OCT 09 2003 UNITED STATES PATENT AND TRADEMARK OFFICE

FTI LEGAL DEPT.

BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

DOCKETED:

Reconsideration  
Date due: 11/24/03

Ex parte JEAN-PIERRE DATH and WALTER VERMEIREN

MAILED

SEP 24 2003

U.S. PATENT AND TRADEMARK OFFICE  
BOARD OF PATENT APPEALS  
AND INTERFERENCES

Appeal No. 2003-1185  
Application No. 09/594,059

ON BRIEF

Before WARREN, WALTZ, and DELMENDO, Administrative Patent Judges.  
WALTZ, Administrative Patent Judge.

#### DECISION ON APPEAL

This is a decision on an appeal from the primary examiner's refusal to allow claims 1 through 14 and 16 through 33, the only claims pending in this application, as amended subsequent to the final rejection (see the amendment dated May 15, 2002, Paper No. 12, entered as per the Advisory Action dated June 5, 2002, Paper No. 13). We have jurisdiction pursuant to 35 U.S.C. § 134.

According to appellants, the invention is directed to the cracking of an olefin-rich feedstock in the presence of hydrogen to

produce a product having a similar olefin content (within  $\pm 15\%$ ) but with a different olefin distribution (Brief, page 3).<sup>1</sup>

Appellants state that the claims do not stand or fall together (Brief, page 5). As noted by the examiner (Answer, page 2, ¶(7)), appellants present reasonably specific, substantive arguments for the separate patentability of several groups of claims (e.g., Brief, pages 9-11). Therefore, for each rejection, we consider the claims separately to the extent that appellants have presented separate arguments. See 37 CFR § 1.192(c)(7)(2000); *In re McDaniel*, 293 F.3d 1379, 1383, 63 USPQ2d 1462, 1465 (Fed. Cir. 2002). A copy of illustrative independent claim 1 is reproduced below:

1. A process for cracking an olefin-rich hydrocarbon feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing olefins having a first composition of one or more olefinic components with a crystalline silicate catalyst to produce an effluent having a second composition of one or more olefin components in which the olefin distribution is different from the olefin distribution of said feedstock, the feedstock and the effluent having substantially the same olefin content by weight therein wherein the olefin content of the effluent is within  $\pm 15\%$  of the olefin content of the feedstock, the feedstock contacting the catalyst in the presence of hydrogen for enhancing the stability of the catalyst.

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<sup>1</sup>We note that, in addition to the related appeals listed on page 2 of the Brief, the examiner should also consider commonly-assigned, same inventive entity S.N. 09/596,356 (Appeal No. 2003-1163).

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Application No. 09/594,059

The examiner has relied upon the following references as evidence in support of the rejections on appeal:

Haag et al. (Haag)                      0 034 444                      Aug. 26, 1981  
(published European Patent Application)

Colombo et al. (Colombo)              0 109 060                      May 23, 1984  
(published European Patent Application)

Claims 1-3, 16, 18-20 and 22-25 stand rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as unpatentable over Haag (Answer, page 3). Claims 4, 5, 12, 13, 17 and 21 stand rejected under 35 U.S.C. § 103(a) as unpatentable over Haag (Answer, page 4). Claims 6-11, 14, and 26-33 stand rejected under 35 U.S.C. § 103(a) as unpatentable over Haag in view of Colombo (Answer, page 5).<sup>2</sup> We reverse the rejection based on section 102(b) but affirm all of the rejections based on section 103(a) essentially for the reasons stated in the Answer and those reasons set forth below. Accordingly, the decision of the examiner is affirmed.

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<sup>2</sup>The final rejection of claims 15, 31 and 32 under the second paragraph of 35 U.S.C. § 112 has been withdrawn by the examiner in view of the amendment subsequent to the final rejection (see the amendment dated May 15, 2002, Paper No. 12, entered as per the Advisory Action dated June 5, 2002, Paper No. 13).

OPINION

A. *The Rejection under § 102(b)/§ 103(a)*

The examiner finds that Haag discloses a process for cracking an olefinic feedstock in the presence of hydrogen and a zeolitic catalyst, such as ZSM-5, to produce lower molecular weight products (Answer, page 3, citing Haag, the abstract, and page 20, l. 22 through page 21, l. 17). The examiner finds that Haag is silent as to what kind of hydrocarbon compounds are produced. *Id.* However, the examiner concludes that these lower molecular weight products must inherently be the same as appellants' claimed products since the Haag process is operated under the same reaction conditions for the same feedstock using the same catalyst. *Id.* Accordingly, the examiner considers a rejection under sections 102/103 to be appropriate, citing *In re Best*, 195 USPQ at 433. *Id.* We disagree.

To support a rejection based on inherency, the examiner must provide a basis in fact or technical reasoning to reasonably support a determination that the claimed process would have necessarily flowed from the teachings of the prior art, not that it would have probably occurred. See *In re Robertson*, 167 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999); *In re Sussman*, 141 F.2d 267, 269-70, 60 USPQ 538, 540-41 (CCPA 1944). The examiner finds that "Haag clearly discloses a hydro-cracking of olefins to

produce lower weight substances (the abstract; page 20, line 22 thru page 21, line 17; col. 23 [sic, page 23], lines 5-26)."

Answer, page 6. This factual finding is in error as there is no basis in the cited portions of Haag that support this finding (see the Brief, pages 6-9). Haag discloses the zeolitic cracking of olefins from high to low molecular weight substances (page 20, ll. 22-25; page 21, ll. 12-15). However, the examiner has not specifically identified, and we cannot find, any specific disclosure of Haag to hydrocracking of olefins or cracking of olefins in the presence of hydrogen. We note that the Haag disclosure of catalytic conversion conditions for cracking, which is only one of many conversions disclosed, fails to mention the presence of hydrogen. While Haag does disclose a H<sub>2</sub>/hydrocarbon mole ratio for hydrocracking (page 23, ll. 5-26), there is no specific teaching regarding the hydrocracking of an olefin-rich hydrocarbon feedstock.

For the foregoing reasons, we determine that the examiner has not established a *prima facie* case of anticipation based on the reference evidence. Accordingly, we cannot sustain the examiner's rejection of claims 1-3, 16, 18-20 and 22-25 under 35 U.S.C. § 102(b) as anticipated by Haag.

Next we must consider whether the disclosure of Haag would have suggested the claimed subject matter to one of ordinary skill in this art. See *In re Keller*, 642 F.2d 413, 425, 208 USPQ 871, 881 (CCPA 1981). As noted above, Haag discloses the hydrocracking of hydrocarbons in the presence of zeolite catalysts (abstract; page 20, ll. 22-25; and page 21, ll. 15-17). Therefore the issue becomes whether Haag would have suggested to one of ordinary skill in this art to hydrocrack an olefin feedstock. We determine that one of ordinary skill in this art would have reasonably used olefin feedstocks in the hydrocracking process of Haag in view of the related disclosures of Haag at page 20, ll. 22-25, page 21, ll. 12-17, and page 23, ll. 5-26. These cited disclosures teach that the "hydrocarbon conversion processes" include cracking and hydrocracking (pages 20 and 21), that olefins can be cracked from high to low molecular weight substances (page 21), and that the "conversion of hydrocarbon compounds" applies to cracking and hydrocracking (page 23; see line 15 which has antecedence in line 5; the "conversion of hydrocarbons" in line 5 refers back to the olefins listed at page 21, l. 14). Accordingly, we determine that Haag would have suggested to one of ordinary skill in this art hydrocracking of olefin feedstocks using silicalite/zeolite catalysts.



Appellants argue that the term "hydrocracking" is commonly understood to be the cracking of petroleum or petroleum products in the presence of hydrogen, citing pages 613 and 889 of *Hawley's Condensed Chemical Dictionary* (Hawley's) as evidence to support this statement (Brief, pages 6-7). This argument is not persuasive. Appellants have only submitted evidence that hydrocracking is directed to petroleum or petroleum products, but have not established that these products do not include olefins. As noted by the examiner, appellants have admitted that petroleum products may be olefins (Answer, page 6, citing the Brief, page 7, ll. 3-6). Additionally, we note that the examiner has presented evidence that the art recognizes that petroleum and petroleum products include olefins (Answer, page 6) and this evidence has not been contested by appellants.

Appellants argue that Haag fails to disclose that the effluent and the product have olefin contents within the range of  $\pm 15\%$  as recited in the claims (Brief, page 7). This argument is not persuasive since Haag teaches operating conditions that are similar or overlap those disclosed and claimed by appellants (see page 23). Accordingly, the optimization of reaction conditions to produce a desired result would have been well within the ordinary skill in this art, absent a showing of unexpected results. See *In re*

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*Woodruff*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Appellants argue that there is nothing in Haag which would even remotely suggest the use of hydrogen to enhance the stability of the catalyst (Brief, page 8). This argument is not well taken since the prior art need not use hydrogen for the same purpose as appellants. Cf. *In re Kemps*, 97 F.3d 1427, 1430, 40 USPQ2d 1309, 1311 (Fed. Cir. 1996).

With regard to claims 2, 3, 23 and 24, appellants argue that the claimed hydrogen partial pressures cannot be found in Haag (Brief, page 9). However, we adopt our remarks from above concerning the obviousness of hydrocracking an olefin feedstock in the presence of a zeolite catalyst. The determination of optimum partial pressures of hydrogen would have been within the ordinary skill in this art, especially in view of the amounts of hydrogen taught by Haag (page 20, l. 29-page 21, l. 2; page 23, ll. 24-26). See *In re Woodruff*, *supra*.

With regard to claims 16-19, appellants argue that the very broad ranges found in Haag would not anticipate the "very narrow ranges" set forth in the claims (Brief, paragraph bridging pages 9-10). This argument is not persuasive since the rejection is based on obviousness, not anticipation. As noted by the examiner

(Answer, page 7), at least some of the reaction parameters overlap. The determination or optimization of such parameters would have been well within the ordinary skill in this art. See *In re Woodruff*, *supra*.

For the foregoing reasons and those stated in the Answer, we determine that the examiner has established a *prima facie* case of obviousness in view of the reference evidence. Based on the totality of the record, including due consideration of appellants' arguments and evidence, we determine that the preponderance of evidence weighs most heavily in favor of obviousness within the meaning of section 103 (a). Accordingly, we affirm the rejection of claims 1-3, 16, 18-20 and 22-25 under 35 U.S.C. § 103(a) over Haag.

*B. The Rejection under § 103(a) over Haag*

We adopt the examiner's factual findings and our remarks about Haag from above. With regard to claims 4, 5, 12 and 13, appellants argue that Haag does not disclose the use of hydrogen in a process of cracking an olefin-rich feedstock (Brief, pages 10-11). As discussed above, we have determined that Haag suggested hydrocracking of olefins in the presence of a zeolite catalyst. With regard to claim 21, appellants argue that Haag does not even address the subject of dienes (Brief, page 11). This argument is

not persuasive since appellants admit that it was known in the prior art to remove dienes if present in the olefin feedstock prior to any catalytic cracking process (specification, page 5, ll. 19-30).<sup>3</sup> Accordingly, limiting the diene content in an olefin feedstock prior to cracking or hydrocracking would have been suggested to one of ordinary skill in this art.

For the foregoing reasons and those set forth in the Answer, we determine that the examiner has established a *prima facie* case of obviousness in view of the reference evidence. Based on the totality of the record, including due consideration of appellants' arguments, we determine that the preponderance of evidence weighs most heavily in favor of obviousness within the meaning of section 103(a). Accordingly, we affirm the examiner's rejection of claims 4, 5, 12, 13, 17 and 21 under 35 U.S.C. § 103(a) over Haag.

*C. The Rejection over Haag in view of Colombo*

In addition to the findings from Haag as discussed above and in the Answer, the examiner finds that Colombo discloses a cracking

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<sup>3</sup>Admitted prior art in an applicant's specification may be used in determining the patentability of a claimed invention. See *In re Nomiya*, 509 F.2d 566, 570-71, 184 USPQ 607, 611-12 (CCPA 1975). Consideration of the prior art cited by the examiner may include consideration of the admitted prior art found in applicant's specification. See *In re Davis*, 305 F.2d 501, 503, 134 USPQ 256, 258 (CCPA 1962).

process catalyzed by silicalite having a Si/Al ratio of 175 to infinity that will produce a high yield of propylene (Answer, page 5). From these findings, the examiner concludes that it would have been obvious to have modified the Haag process by using the silicalite catalyst taught by Colombo for its high yield of propylene (*id.*). We agree.

Appellants argue that Colombo does not disclose the cracking of an olefin-rich feedstock in the presence of hydrogen (Brief, page 11). Appellants are correct in their argument. However, Haag does disclose/suggest cracking or hydrocracking olefin feedstocks with a silicalite catalyst where the Si/Al mole ratio is at least 12, with embodiments as high as 70 to 78.4 (see page 32, l. 4). Colombo similarly teaches the cracking of olefins into propylene using zeolite catalysts such as silicalites where the Si/Al mole ratio is greater than 350 (abstract; page 1, ll. 25-35). Colombo teaches that use of these high Si/Al mole ratio catalysts produces high yields of propylene while extending the life of the catalyst (page 1, ll. 16-24; page 2, ll. 34-36). Accordingly, we agree with the examiner that it would have been well within the ordinary skill in this art to substitute the catalysts of Colombo for the similar silicalite catalysts in the hydrocracking process of Haag with the

expectation of higher yields of propylene and a longer catalyst life.

With respect to claims 10 and 11, appellants argue that one of ordinary skill in the art would not, viewing only the Haag and Colombo references, attempt to replace the zeolites in Haag which have appreciable aluminum contents with the silicalites in Colombo which have no aluminum content, i.e., a Si/Al ratio of infinity. (Brief, page 12). This argument is not well taken for the reasons stated above, namely one of ordinary skill in this art would have been motivated to use the silicalite catalysts of Colombo in the process of Haag to increase the propylene yield and extend the life of the catalysts. We note that the Si/Al mole ratio of Haag is open-ended, i.e., at least 12, thus encompassing high mole ratios such as those taught by Colombo. Furthermore, appellants are attempting to limit Colombo to the examples which have Si/Al mole ratios of infinity. However, a reference is not limited to its examples but is available for all that its disclosure would teach or suggest to one of ordinary skill in the art. See *In re Widmer*, 353 F.2d 752, 757, 147 USPQ 518, 523 (CCPA 1965).

With respect to claims 6-9 and 26-29, appellants argue that neither Haag nor Colombo disclose the addition of ethylene to the feedstock as called for by these claims (Brief, page 12). This

argument is not persuasive since Colombo teaches that a desired product of cracking would include ethylene (page 1, ll. 14-15). It would have been well within the ordinary skill in this art to add the desired product to the feedstock to help drive the cracking to completion. With respect to claims 7 and 28, appellants argue that there is nothing in the references which would render obvious the recycle of ethylene to the feedstock (Brief, page 13). This argument is not persuasive since Colombo teaches recycle of higher olefins (Answer, page 6; Colombo, page 3, ll. 28-30) and the recycling of any unreacted olefinic reactants would have been obvious to decrease the cost of the feedstock and increase the yield of the product.

With respect to claims 14 and 30, appellants argue that Colombo does not disclose a propylene yield as required by these claims (Brief, page 13). However, appellants have not contested the examiner's finding that Colombo discloses a yield of propylene of more than 30% (Answer, page 8). Regardless, the yield of propylene is dependent on many factors, which can be optimized by one of ordinary skill in this art. See *In re Woodruff*, *supra*.

With respect to appellants' recitation of the limitations of claims 25-29, 31 and 32 on pages 14-15 of the Brief, we adopt our

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Application No. 09/594,059

remarks from above as all of appellants' arguments have been previously answered.

For the foregoing reasons and those stated in the Answer, we determine that the examiner has established a *prima facie* case of obviousness in view of the reference evidence. Based on the totality of the record, including due consideration of appellants' arguments, we determine that the preponderance of evidence weighs most heavily in favor of obviousness. Accordingly, the rejection of claims 6-11, 14, 26-29 and 30-33 under 35 U.S.C. § 103(a) over Haag in view of Colombo is affirmed.

*D. Summary*

The rejection of claims 1-3, 16, 18-20 and 22-25 under 35 U.S.C. § 102(b) over Haag is reversed.

The rejection of claims 1-3, 16, 18-20 and 22-25 under 35 U.S.C. § 103(a) over Haag is affirmed.

The rejection of claims 4, 5, 12, 13, 17 and 21 under 35 U.S.C. § 103(a) over Haag is affirmed.

The rejection of claims 6-11, 14, 26-29 and 30-33 under 35 U.S.C. § 103(a) over Haag in view of Colombo is affirmed.


The decision of the examiner is affirmed.



Appeal No. 2003-1185  
Application No. 09/594,059

No time period for taking any subsequent action in connection with this appeal may be extended under 37 CFR § 1.136(a).

**AFFIRMED**

  
CHARLES F. WARREN  
Administrative Patent Judge

THOMAS A. WALTZ  
Administrative Patent Judge

BOARD OF PATENT  
APPEALS  
AND  
INTERFERENCES

*Romulo H. Delmendo*  
ROMULO H. DELMENDO  
Administrative Patent Judge

TAW/jrg

Appeal No. 2003-1185  
Application No. 09/594,059

FINA TECHNOLOGY INC  
PO BOX 674412  
HOUSTON, TX 77267-4412

F-716

The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

**DOCKETED,***Reconsideration*  
Date due: 8/31/03

Paper No. 28

**UNITED STATES PATENT AND TRADEMARK OFFICE****BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES****RECEIVED**

APR 4 2003

*Ex parte* JEAN-PIERRE DATH, LUC DELORME, FTI LEGAL DEPT.  
JACQUES-FRANCOIS GROOTJANS, XAVIER VANHAEREN  
and WALTER VERMEIREN

Appeal No. 2002-1010  
Application No. 09/206,210

**MAILED**

MAR 31 2003

F716

HEARD: March 20, 2003

**PAT. & T.M. OFFICE  
BOARD OF PATENT APPEALS  
AND INTERFERENCES**

Before WARREN, WALTZ and DELMENDO, Administrative Patent Judges.

WALTZ, Administrative Patent Judge.

**DECISION ON APPEAL**

This is a decision on an appeal from the primary examiner's refusal to allow claims 9, 11, 13, 14 and 18 as amended subsequent to the final rejection.<sup>1</sup> Claims 1 through 8 are the only other claims pending in this application and stand withdrawn from further consideration by the examiner as directed to a non-

<sup>1</sup>An amendment dated July 5, 2001, Paper No. 16, subsequent to the final rejection, was entered by the examiner as noted in the Advisory Action dated July 25, 2001, Paper No. 17.

Appeal No. 2002-1010  
Application No. 09/206,210

Page 2

elected invention (Brief, page 2; Answer, page 2, ¶13).<sup>2</sup> We have jurisdiction pursuant to 35 U.S.C. § 134.

According to appellants, the invention is directed to a process for the catalytic cracking of olefins in which the feedstock is contacted with an MFI crystalline silicate catalyst having a silicon/aluminum atomic ratio of 180 to 1000, where the catalyst has been prepared by a process in which aluminum atoms have been removed from throughout the crystalline silicate framework (Brief, page 3). Claim 9 is illustrative of the invention and is reproduced below:

9. A process for the catalytic cracking of olefins in a hydrocarbon feedstock which is selective towards light olefins in the effluent, the process comprising<sup>3</sup> contacting a hydrocarbon feedstock containing olefins having a first composition of at least one olefinic component with a MFI crystalline silicate catalyst having a silicon/aluminum atomic ratio of from 180 to 1000 to produce an effluent having a second composition of at least one olefinic component, with the feedstock and the effluent having substantially the same olefin content by weight therein, the catalyst having been produced by heating the catalyst in steam to remove aluminum from a crystalline silicate framework of the catalyst and extracting aluminum from the catalyst by contacting the catalyst with a complexing agent for aluminum to remove, from pores of the framework, aluminum deposited therein during the steaming step, thereby to increase the silicon/aluminum atomic ratio

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<sup>2</sup>All reference to and citation from the Brief is to the Substitute Brief dated Sep. 10, 2001, Paper No. 19.

<sup>3</sup>This term apparently should read "comprising" (see the specification, page 7).

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Application No. 09/206,210

Page 3

of the catalyst, and calcining the catalyst at elevated temperature.

The examiner has relied upon the following references as evidence of obviousness:

Bowes et al. (Bowes)	4,876,411	Oct. 24, 1989
Kuehl et al. (Kuehl)	4,954,243	Sep. 04, 1990
Colombo et al. (EP '060) (published European Patent Application)	0 109 060	May 23, 1984

The claims on appeal stand rejected under 35 U.S.C. § 103(a) as unpatentable over EP '060 in view of Bowes and Kuehl (Answer, page 3). The claims on appeal stand provisionally rejected under the judicially created doctrine of obviousness-type double patenting over (1) claims 1-16 of copending application no. 09/206,207 (Answer, page 5); (2) claims 1-16 of copending application no. 09/206,208 (Answer, page 6); (3) claims 1-26 of copending application no. 09/206,216 (*id.*); and (4) claims 1-16 of copending application no. 09/206,218 (Answer, sentence bridging pages 6-7).

We summarily *affirm* all of the examiner's provisional rejections based on obviousness-type double patenting for the reasons stated in the Answer. We reverse the examiner's rejection based on section 103(a) essentially for the reasons stated in the Brief, Reply Brief, and those reasons set forth below. Therefore the decision of the examiner to reject the claims on appeal is affirmed.

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Application No. 09/206,210

Page 4

*A. The Rejections based on Obviousness-type Double Patenting*

Appellants present no arguments against the examiner's provisional rejections based on the judicially created doctrine of obviousness-type double patenting (Brief, page 5). Accordingly, we presume that appellants acquiesce to these provisional rejections and thus summarily affirm all of the examiner's provisional rejections based on the judicially created doctrine of obviousness-type double patenting for the reasons advanced by the examiner in the Answer. See *In re Wetterau*, 356 F.2d 556, 557-58, 148 USPQ 499, 500-01 (CCPA 1966); cf. *Ex parte Karol*, 8 USPQ2d 1771, 1773-74 (Bd. Pat. App. & Int. 1988).

*B. The Rejection based on 35 U.S.C. § 103(a)*

The examiner finds that EP '060 discloses a process for the conversion of olefins to propylene by contacting the feed with a zeolite catalyst, where this catalyst has a Si/Al ratio of greater than 350 "which meets the instantly claimed values." Answer, page 4.<sup>4</sup> The examiner finds that EP '060 does not disclose or teach the preparation of the zeolite catalyst as

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<sup>4</sup>As noted by the examiner on pages 9 and 14 of the Answer, the "greater than 350" mole ratio of Si/Al disclosed by EP '060 is equivalent to an atomic ratio for Si/Al of "greater than 175."

Appeal No. 2002-1010  
Application No. 09/206,210

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claimed by appellants but finds that there is a reasonable basis to infer that the catalyst of the reference is identical or only slightly different from those claimed (Answer, pages 4 and 8-9).

The examiner applies Bowes and Kuehl for their teaching of methods of making dealuminated zeolites for use in cracking processes, which methods include the steps of steaming, extraction of aluminum with a complexing agent, and calcination (Answer, page 4). From these findings, the examiner concludes that it would have been obvious to one of ordinary skill in the art to have used either the dealuminated zeolites of Kuehl or Bowes in the process of EP '060 because these secondary references teach that dealuminated zeolite catalysts may be used in cracking processes and all the references are directed to "high Si MFI type zeolites." Answer, paragraph bridging pages 4-5. We disagree.

The mere finding that the silica/alumina atomic ratios of EP '060 and the claimed atomic ratio are similar (i.e., overlapping) is not *per se* sufficient evidence to support the examiner's "reasonable basis" that the catalysts of the prior art and the claims are identical or substantially identical. See *In re Spada*, 911 F.2d 705, 708, 15 USPQ2d 1655, 1657-58 (Fed. Cir. 1990); *In re Best*, 562 F.2d 1252, 1255, 195 USPQ 430, 433, (CCPA 1997). Catalysts may have the identical silica/alumina atomic

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Application No. 09/206,210

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ratio but differ markedly in structure and composition. As correctly argued by appellants (Brief, page 6; Reply Brief, page 3) and admitted by the examiner (Answer, page 4), EP '060 does not address even broadly the dealumination of its zeolite catalyst. Accordingly, we determine that the examiner has not presented a *prima facie* case of obviousness over EP '060 alone (*id.*).

Appellants argue that the secondary references to Bowes and Kuehl are specifically directed only to surface treatment of the zeolite, i.e., only removing aluminum from the surface of the catalyst structure (Brief, pages 6-7; Reply Brief, page 3). Although appellants cite portions of Bowes and Kuehl that refer to this surface treatment, both references suggest that some aluminum may be removed from the internal pore structure of the catalyst. See Kuehl, col. 25-34, where the reference teaches that the EDTA chelating agent does not go into the zeolite pores but does remove aluminum ions migrating out of the pores by complexing. See Bowes, col. 8, ll. 20-29, where the reference teaches that steaming partially or completely decomposes the template material and, at the same time, removes framework (zeolitic) aluminum, preferentially aluminum located at the surface of the zeolite (thus implicitly suggesting that some internal aluminum is removed).



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Application No. 09/206,210

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However, even assuming *arguendo* that Bowes and Kuehl disclose or suggest the same method recited in the claims on appeal for production of the MFI crystalline silicate catalyst (i.e., steaming and dealumination to remove aluminum from the pores), we agree with appellants that the examiner has not provided any convincing reason or motivation for combining these references with the process of EP '060 (Brief, page 9).<sup>5</sup> See *In re Dembiczak*, 175 F.3d 994, 999, 50 USPQ2d 1614, 1617 (Fed. Cir. 1999). The only "general" statements of motivation supplied by the examiner are that all of the references disclose zeolites that may be used in cracking and all references are directed to "high Si MFI type zeolites." Answer, paragraph bridging pages 4-5. These general statements are not convincing, since EP '060 is directed to zeolite catalysts with a Si/Al atomic ratio of 175 or greater, while Kuehl is directed to catalysts with Si/Al atomic ratios of greater than 6 (col. 2, ll. 63-64; col. 12, ll. 59-63) with examples as high as 35 (Examples 6, 7 and 8), and Bowes teaches activity "even when the silica to aluminum mole ratio exceeds 30 [atomic ratio 15]," with examples as high as 54. See col. 3, ll. 40-43, and col. 11, l. 61, Table 2. Therefore we determine that the examiner has not established why one of

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<sup>5</sup>In view of our decision, we need not discuss appellants' reference evidence (Exhibit B, Brief, page 9) or objective evidence of "substantially improved results" (Brief, page 13).

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Application No. 09/206,210

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ordinary skill in this art would have used the steaming and dealumination processes of Bowes or Kuehl, directed to relatively low Si/Al atomic ratios, with the process of EP '060 when this reference already has a desired high Si/Al atomic ratio catalyst of 175 or greater.

For the foregoing reasons, we determine that the examiner has not established a *prima facie* case of obviousness in view of the reference evidence. Accordingly, the rejection of the claims on appeal under 35 U.S.C. § 103(a) over EP '060 in view of Bowes or Kuehl is reversed.

C. Summary

The provisional rejections of claims 9, 11, 13-14 and 18 under the judicially created doctrine of obviousness type double patenting over (1) claims 1-16 of application no. 09/206,207; (2) claims 1-16 of application no. 09/206,208; (3) claims 1-26 of application no. 09/206,216; and (4) claims 1-16 of application no. 09/206,218 are summarily affirmed.

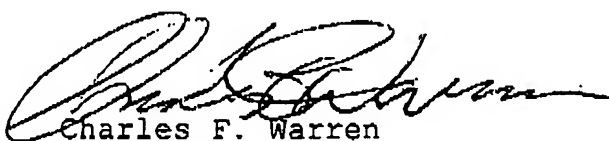
The rejection of claims 9, 11, 13-14 and 18 under 35 U.S.C. § 103(a) over EP '060 in view of Bowes or Kuehl is reversed.

The decision of the examiner is affirmed.

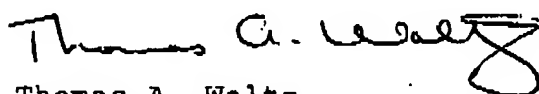
Appeal No. 2002-1010  
Application No. 09/206,210

Page 9

No time period for taking any subsequent action in  
connection with this appeal may be extended under 37 CFR  
§ 1.136(a).

**AFFIRMED**

Charles F. Warren  
Administrative Patent Judge



Thomas A. Waltz  
Administrative Patent Judge

BOARD OF PATENT

APPEALS AND

INTERFERENCES



Romulo H. Delmendo  
Administrative Patent Judge

TAW/eld

Appeal No. 2002-1010  
Application No. 09/206,210

Page 10

Fina Technology Inc.  
P.O. Box 674412  
Houston, TX 77267-4412

The opinion in support of the decision being entered today was **not** written for publication and is **not** binding precedent of the Board.

Paper No. 23

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

Ex parte JEAN-PIERRE DATH, LUC DELORME,  
JACQUES-FRANCOIS GROOTJANS, XAVIER VANHAEREN,  
and WALTER VERMEIREN

Appeal No. 2002-1739  
- Application No. 09/205,559

HEARD: March 20, 2003

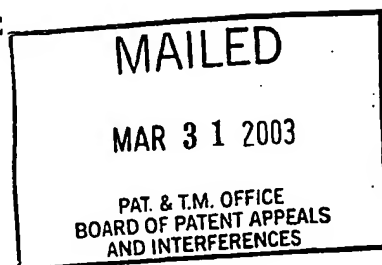
Before WARREN, WALTZ, and DELMENDO, Administrative Patent Judges.  
WALTZ, Administrative Patent Judge.

#### DECISION ON APPEAL

This is a decision on an appeal from the primary examiner's final rejection of claims 1, 3, 5 through 13 and 16, which are the only claims pending in this application.<sup>1</sup> We have jurisdiction pursuant to 35 U.S.C. § 134.

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<sup>1</sup>An amendment dated June 27, 2001, Paper No. 11, submitted subsequent to the final rejection, was entered as per the Advisory Action dated July 2, 2001, Paper No. 12.



Appeal No. 2002-1739  
Application No. 09/205,559

According to appellants, the invention is directed to a process for the catalytic cracking of an olefin-rich feedstock to produce an effluent with an olefin content of lower molecular weight than the olefin content of the feedstock (Brief, page 2). A further understanding of the invention may be found from illustrative independent claim 1, reproduced below:

1. A process for the catalytic cracking of an olefin-rich feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing at least one olefin, with a MFI-type crystalline silicate having a silicon/aluminum atomic ratio within the range of 300-500 at an inlet temperature of from 500 to 600°C, at an olefin partial pressure of from 0.1 to 2 bars and the feedstock being passed over the catalyst at an LHSV of from 10 to 30h<sup>-1</sup>, to produce an effluent with an olefin content of lower molecular weight than that of the feedstock.

Appellants state that the claims do not stand or fall together (Brief, page 4) and present reasonably specific, substantive reasons for the separate patentability of claims 1, 7-9, 11 and 12 in the argument section of the Brief (e.g., see page 12). Accordingly, we consider these claims separately to the extent they have been separately argued. See 37 CFR § 1.192(c)(7)(8)(2000).

The examiner has relied upon the following reference as evidence of obviousness:

Colombo et al. (EP '060)      0 109 060  
(published European Patent Application)

May 23, 1984

Appeal No. 2002-1739  
Application No. 09/205,559

Appellants have relied upon the following references as  
countervailing evidence of non-obviousness (Brief, pages 3-4):

Meier et al. (Exhibit B), *Atlas of Zeolite Structure Types*, pp.  
1-12 and 89-93, Structure Commission of the International Zeolite  
Association, publishers, 1978; and

Flanigen et al. (Exhibit C), "Silicalite, a new hydrophobic  
crystalline silica molecular sieve," pp. 512-516, *Nature*, Vol.  
271, Feb. 9, 1978.

The claims on appeal stand rejected under 35 U.S.C. § 103(a)  
as unpatentable over EP '060 (Answer, page 3).<sup>2</sup> We affirm this  
rejection essentially for the reasons stated in the Answer and  
those reasons set forth below.

#### OPINION

The examiner finds that EP '060 discloses a process of  
cracking olefins having from 4 to 12 carbons to produce propylene  
by use of zeolitic catalysts including the MFI-type catalysts of  
silicalite or ZSM-5 having a silicon/aluminum (Si/Al) atomic  
ratio of greater than 175 at temperatures of 400 to 600°C. at a  
space velocity of from 5 to 200/hr (Answer, page 3, citing the  
abstract and page 3, ll. 18-20, of EP '060). The examiner finds  
that EP '060 does not specifically disclose a MFI-type catalyst  
having a Si/Al atomic ratio of 300 to 500 as required by claims

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<sup>2</sup>The final rejection of all claims under 35 U.S.C. § 102(b) as  
anticipated by EP '060 has been withdrawn by the examiner (Answer,  
page 4).

1, 11 and 16 but this reference does teach the broad range of 175 to infinity for the Si/Al atomic ratio (*id.*). From these findings, the examiner concludes that it would have been obvious to one of ordinary skill in this art to have used the process of EP '060 with MFI-type zeolitic catalysts having a Si/Al atomic ratio of 300 to 500 with the expectation of similar results for any of the disclosed catalysts (*id.*). We agree.

Appellants argue that EP '060 not only fails to disclose the claimed range of 300-500 for the Si/Al atomic ratio but simply refers to a Si/Al atomic ratio of at least 175 to infinity with no upper limit (Brief, page 5). Appellants disagree with the premise that the disclosure of very broad ranges overlapping or encompassing narrow ranges renders the use of such ranges obvious (*id.*). This argument is not well taken. It is well settled patent jurisprudence, as shown by the appellants' own citations to *In re Russell* and *In re Waymouth* (Brief, paragraph bridging pages 5-6) that the disclosure in the prior art of ranges encompassing the narrower ranges of the claims may establish a case of *prima facie* obviousness. See also *In re Woodruff*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990). Appellants may confuse the establishment of a *prima facie* case of obviousness with the consideration of rebuttal evidence since



they allege "unexpectedly superior results" on page 6 of the Brief. Once a *prima facie* case of obviousness has been established, then the burden shifts to appellants to present evidence of the criticality of the narrower claimed ranges, usually by the comparison of the ranges to show unexpected results. See *In re Oetiker*, 977 F.2d 1443, 1445, 24 USPQ2d 1443, 1444 (Fed. Cir. 1992); *In re Woodruff*, *supra*.

Appellants argue that EP '060 does not disclose or suggest the particular claimed combination of parameters but discloses "broad ranges" of olefin partial pressure, space velocity and temperature (Brief, page 6). Appellants further argue that Example 36, discussed by the examiner, does show a space velocity within the claimed range but also shows a Si/Al atomic ratio outside of the claimed range and does not indicate that the molecular weight of the olefin content of the effluent is lower than the molecular weight of the olefin content of the feedstock as required by the claims (Brief, pages 7 and 13).

These arguments are not persuasive. The broad ranges disclosed by EP '060 would have suggested to one of ordinary skill in this art that any values within these broad ranges, inclusive of the ranges claimed by appellants, would have been expected to yield similar results in the process of EP '060 (see

Appeal No. 2002-1739  
Application No. 09/205,559

the Answer, page 3). Even as argued by appellants (Brief, page 6), the space velocity taught by EP '060 is very similar to the claimed range when pressure considerations are considered.<sup>3</sup> Furthermore, the temperature range disclosed by EP '060 is not much broader than, and totally encompasses, the claimed range. Although Example 36 discloses cracking temperatures, space velocities, and olefin partial pressures within the claimed ranges (EP '060, page 7), the examiner recognizes that the EP '060 process is not limited to its examples (Answer, page 4). See *In re Widmer*, 353 F.2d 752, 757, 147 USPQ 518, 523 (CCPA 1965). As also indicated by the examiner, other examples and tables evidence that the molecular weight of the olefin content of the effluent is lower than the molecular weight of the olefin content of the feedstock (Answer, paragraph bridging pages 4-5, citing examples 8-23). This evidence has not been contested by appellants (see the Reply Brief in its entirety).

Appellants submit that Exhibit B shows that some of the zeolites disclosed by EP '060 are not MFI-type silicates, while it is "presumed" that silicalite and ZSM-5 are MFI-type catalysts

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<sup>3</sup>EP '060 teaches that if silicalite-1 is used and the pressure is atmospheric, the space velocity must be lower than 50/hr (page 2, ll. 3-6).

Appeal No. 2002-1739  
Application No. 09/205,559

(Brief, page 10).<sup>4</sup> However, appellants argue that every example in EP '060 directed to a silicalite catalyst specifies a Si/Al atomic ratio of infinity and thus a "fair reading" of EP '060 is that the Si/Al atomic ratio is of no significance (*id.*). This argument is not well taken since, as noted above, a reference is not limited to its examples but is available for all that it discloses and suggests to one of ordinary skill in the art. See *Widmer, supra*. To consider a "fair reading" of EP '060 to teach that the Si/Al atomic ratio is of no significance would be to ignore the specific teaching of the reference regarding the lower limits of the Si/Al atomic ratio range.

Appellants argue that, based upon the data presented in Example 36 of EP '060, the conclusion clearly is that the propylene content is below the 30-50% range required in claims 8 and 11 (Brief, page 12). Again we note that a reference is not limited to any one example. See the Answer, page 5, where the examiner cites Example 24 in Table 4 as showing a propylene yield of 36%.

Appellants' argument regarding the limitations of claims 7 and 12 (Brief, pages 12-13) is believed adequately answered by

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<sup>4</sup>A discussion of Exhibit C is unnecessary to this decision as this Exhibit has only been cited by appellants to provide a description of silicalite (Brief, page 4).

the examiner (Answer, page 5). Therefore we adopt these comments as our own. Similarly, with respect to the argument concerning the limitation of claim 9 (Brief, page 13), we adopt the examiner's comments on page 6 of the Answer. We note that Example 10 is directed to a boronite catalyst (see the Reply Brief, page 3), but we note that the amounts of olefins in the effluent would have been within the control of one of ordinary skill in this art depending on the reaction parameters.

For the foregoing reasons and those stated in the Answer, we determine that the examiner has established a *prima facie* case of obviousness in view of the reference evidence. Appellants submit that any *prima facie* case of obviousness has been overcome by the experimental work found in appellants' specification (Brief, pages 8-10, 11; Reply Brief, pages 1-3). Accordingly, we begin anew and weigh the evidence for and against obviousness. See *Oetiker and Woodruff, supra*.

Appellants argue that the data found in Examples 1 and 2, and shown in Figure 1, is reasonably commensurate in scope with the claimed range of 300-500 Si/Al atomic ratio and clearly shows unexpected results (Brief, pages 8-10). Appellants submit that all other variables were kept constant except for the Si/Al atomic ratio (Brief, page 11; Reply Brief, page 2).

Appeal No. 2002-1739  
Application No. 09/205,559

We determine that appellants' evidence is not persuasive of non-obviousness for the following reasons. The burden of establishing unexpected results rests with the party submitting these results. See *In re Klosak*, 455 F.2d 1077, 1080, 173 USPQ 14, 16 (CCPA 1972). The results shown in Examples 1 and 2 of the specification have not been characterized as "unexpected," nor has the increase in propylene yield shown to be significant to one of ordinary skill in this art (approximately an increase from 31 to 38% propylene; see Figure 1). See *In re Klosak*, *supra*; cf. *Ex parte Gelles*, 22 USPQ2d 1318, 1319 (Bd. Pat. App. & Int. 1992). Finally, as noted by appellants (Brief, pages 8-9), objective evidence of non-obviousness must be reasonably commensurate in scope with the claimed subject matter. See *In re Boesch*, 617 F.2d 272, 276, 205 USPQ 215, 219 (CCPA 1980). This is especially so in the catalyst art where the results cannot be characterized as predictable. See *In re Mercier*, 515 F.2d 1161, 1167-68, 185 USPQ 774, 779 (CCPA 1975). Although it is arguable that the Si/Al atomic ratios of 300, 350 and 490 are representative of the claimed range in the unpredictable catalyst art, the other reaction parameters are clearly not commensurate in scope with the claimed subject matter. See Examples 1 and 2, where only ZSM-5 catalysts are tested (not any silicalites), at

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Application No. 09/205,559

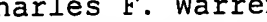
reaction parameters of atmospheric pressure, inlet temperature of 580°C., and a space velocity of "around" 25/hr (see the specification, page 17). The claims on appeal are not so limited with respect to the catalysts employed, the reaction temperatures, space velocities and olefin partial pressures.

Based on the totality of the record, including due consideration of appellants' evidence and arguments, we determine that the preponderance of the evidence weighs most heavily in favor of obviousness within the meaning of section 103(a). Accordingly, the decision of the examiner to reject the claims on appeal under 35 U.S.C. § 103(a) over EP '060 is affirmed.

Appeal No. 2002-1739  
Application No. 09/205,559

No time period for taking any subsequent action in connection with this appeal may be extended under 37 CFR § 1.136(a).

**AFFIRMED**

  
Charles F. Warren )  
Administrative Patent Judge )

Thomas A. Waltz  
Administrative Patent Judge

BOARD OF PATENT  
APPEALS  
AND  
INTERFERENCES

*Romulo H. Delmendo*  
Romulo H. Delmendo  
Administrative Patent Judge

TAW/tdl

Appeal No. 2002-1739  
Application No. 09/205,559

Fina Technology Inc.  
P.O. Box 674412  
Houston, TX 77267-4412



The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

Paper No. 25

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS  
- - - - - AND INTERFERENCES - - - - -

Ex parte JEAN-PIERRE DATH, LUC DELORME, JACQUES-FRANCOIS GROOTJANS,  
XAVIER VANHAEREN and WALTER VERMEIREN

Appeal No. 2002-1863  
Application No. 09/206,207

HEARD: March 20, 2003

Before WARREN, WALTZ, and DELMENDO, Administrative Patent Judges.  
WALTZ, Administrative Patent Judge.

DECISION ON APPEAL

This is a decision on an appeal from the primary examiner's final rejection of claims 1, 2, 6 through 9, 12, 13 and 15 through 27, which are the only claims pending in this application.<sup>1</sup> We have jurisdiction pursuant to 35 U.S.C. § 134.

According to appellants, the invention is directed to a process for the production of olefins by the catalytic cracking of

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<sup>1</sup>The amendment dated Sep. 28, 2001, Paper No. 15, subsequent to the final rejection, was entered as per the Advisory Action dated Oct. 12, 2001, Paper No. 16 (see the Brief, page 2; Answer, page 2).

Appeal No. 2002-1863  
Application No. 09/206,207

an olefin-containing feedstock containing at least 100 parts per million (ppm) of an impurity selected from the group consisting of nitrogen, sulfur and oxygen using a pretreated MFI crystalline

catalyst under particular cracking conditions (Brief, page 3). The

invention may be further understood by illustrative independent claim 1, reproduced below:

1. A process for the catalytic cracking of at least one olefin in an olefinic stream containing impurities, the cracking process being selective towards light olefins in the effluent, the process comprising contacting at an inlet temperature of from 500 to 600°C a feedstock olefinic stream containing at least 100 ppm of at least one impurity selected from the group consisting of nitrogen, sulphur and oxygen with a MFI crystalline silicate catalyst, the catalyst having been heated in steam to reduce the tetrahedral aluminum in the crystalline silicate framework and subjected to an aluminum extraction process to remove aluminum from the pores of the crystalline silicate after which the catalyst has a silicon/aluminum atomic ratio of from 180 to 1000, to produce an effluent stream having substantially the same olefinic content by weight as, but a different olefin distribution than, the feedstock contains.

The examiner relies upon the following references as evidence of obviousness:

Eberly, Jr., et al. (Eberly)	3,506,400	Apr. 14, 1970
Glockner et al. (Glockner)	4,078,011	Mar. 07, 1978
Colombo et al. (EP '060)	0 109 060	May 23, 1984
(published European Patent Application)		

Claims 1, 2, 6-9, 12, 13, 15, 17-19 and 27 stand rejected under 35 U.S.C. § 103(a) as unpatentable over EP '060 in view of Eberly (Answer, page 3). Claims 16 and 20-26 stand rejected under

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Application No. 09/206,207

35 U.S.C. § 103(a) as unpatentable over EP '060 in view of Eberly and Glockner (Answer, page 5). Claims 1, 2, 6-9, 12, 13, 15, 17-19 and 27 stand provisionally rejected under the judicially created doctrine of obviousness-type double patenting over claims 1, 2, and 4-10 of copending application no. 09/206,208 (Answer, page 5). The claims on appeal stand provisionally rejected under the judicially created doctrine of obviousness-type double patenting over (1) claims 1-14 of copending application no. 09/206,218 (Answer, page 6); (2) claims 9-14 of copending application no. 09/206,210 (*id.*); and (3) claims 1, 2, 4-10, 12-14, 16-20, 22, 24 and 27 of copending application no. 09/206,216 (Answer, page 7).

We summarily *affirm* all of the examiner's provisional rejections based on obviousness-type double patenting for the reasons stated in the Answer. We *reverse* the examiner's rejections based on section 103(a) essentially for the reasons stated in the Brief, Reply Brief, and those reasons set forth below. Therefore the decision of the examiner to reject the claims on appeal is affirmed.

#### OPINION

*A. The Rejections based on Obviousness-type Double Patenting.*

Appellants do not contest the examiner's provisional rejections based on the judicially created doctrine of obviousness-

type double patenting (Brief, page 6). Appellants state their intention of submitting an appropriate terminal disclaimer when one or more of the copending applications issue as a patent (*id.*). Accordingly, we summarily affirm all of the examiner's provisional rejections based on the judicially created doctrine of obviousness-type double patenting. See *In re Wetterau*, 356 F.2d 556, 557-58, 148 USPQ 499, 500-01 (CCPA 1966); Cf. *Ex parte Karol*, 8 USPQ2d 1771, 1773-74 (Bd. Pat. App. & Int. 1988).

*B. The Rejections based on 35 U.S.C. § 103(a)*

The examiner finds that EP '060 discloses a process for producing olefins by catalytic cracking an olefin feedstock with a zeolitic catalyst such as silicalite or ZSM-5 with a silica/alumina atomic ratio of greater than 175 under reaction conditions encompassing the claimed parameters (Answer, page 3). The examiner recognizes that EP '060 does not disclose, *inter alia*, the claimed pretreatment of the catalyst including steaming and aluminum extraction (Answer, page 4). Therefore, the examiner applies Eberly for its disclosure of a process for treating zeolite by steaming followed by contact with a complexing agent to remove aluminum from the gross structure of the zeolite, thereby increasing the silica/alumina ratio (*id.*). From these findings, the examiner concludes that it would have been obvious to one of

ordinary skill in the art to modify the process of EP '060 "by dealuminating the zeolite to achieve the desired silicon:aluminum atomic ratio as suggested by Eberly because the resulting zeolite will have higher stability." *Id.*

It is incumbent upon the examiner, when proposing a combination or modification of references, to identify some suggestion to combine the references or make the modification. See *In re Mayne*, 104 F.3d 1339, 1342, 41 USPQ2d 1451, 1454 (Fed. Cir. 1997). As correctly argued by appellants (Brief, pages 11-14; Reply Brief, pages 3-4), Eberly is not directed to MFI-type catalysts and only suggests silica/alumina mole ratios much lower than those required by EP '060 (and as required by the claims on appeal). Eberly does disclose that the catalysts are useful in cracking processes (col. 1, ll. 64-71, and col. 9, ll. 55-61) and that higher silica/alumina mole ratios provide greater stability to heat, steam and acid (col. 2, ll. 20-25). However, these "higher" silica/alumina mole ratios suggested by Eberly are ones such as 8:1 to 12:1 (col. 2, ll. 25-34), with examples as high as 29:1 (Table IV, col. 8, l. 11). Eberly teaches heating a catalyst in steam, followed by extraction with EDTA, results in a catalyst with an "extremely high" silica/alumina mole ratio of about 20 (see Table III, col. 7, ll. 18-37). The lowest silica/alumina mole ratio

suggested by EP '060 is 350 (see EP '060, page 1, and the Answer, page 3, converting this value to an atomic ratio of greater than 175). The examiner has not presented any convincing reasoning, suggestion or motivation as to why one of ordinary skill in this art would have modified the process of EP '060, with catalysts already possessing silica/alumina atomic ratios of greater than 175, by the catalyst pretreatment of Eberly when Eberly teaches that silica/alumina mole ratios of 8 through 20 provide sufficiently increased stability. Accordingly, we determine that the examiner has not presented convincing reasons for the proposed combination of references and therefore no case of *prima facie* obviousness has been established.<sup>2</sup> Thus we cannot sustain the examiner's rejection based on the combination of EP '060 and Eberly.

With regard to the rejection of claims 16 and 20-26, the examiner additionally cites Glockner for the disclosure of a process for selectively hydrogenating dienes (Answer, page 5). Therefore Glockner does not remedy the deficiencies discussed above for the combination of EP '060 and Eberly. Additionally, we agree

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<sup>2</sup>Since we determine that no case of *prima facie* obviousness has been established, a discussion of appellants' countervailing evidence of non-obviousness (Exhibits B, C and D attached to the Brief) is unnecessary to this decision.

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Application No. 09/206,207

with appellants (Brief, pages 14-15) that the examiner has not supplied any convincing evidence to support the combination of Glockner with EP '060 and Eberly (see the Answer, page 5). The examiner has not shown any recognition in this art that dienes would be present in the claimed amounts in the feedstock nor any desire in this art to remove these dienes. Accordingly, the combination including Glockner can only have been made in hindsight. See *In re Dembiczak*, 175 F.3d 994, 999, 50 USPQ2d 1614, 1617 (Fed. Cir. 1999).

For the foregoing reasons, we determine that the examiner has not established a *prima facie* case of obviousness in view of the reference evidence. Therefore we reverse the examiner's rejection based on EP '060, Eberly and Glockner.

C. Summary

We reverse the examiner's rejection of claims 1, 2, 6-9, 12, 13, 15, 17-19 and 27 under 35 U.S.C. § 103(a) over EP '060 in view of Eberly. We also reverse the examiner's rejection of claims 16 and 20-26 under 35 U.S.C. § 103(a) over EP '060 in view of Eberly and Glockner.

We affirm the examiner's provisional rejections under the judicially created doctrine of obviousness-type double patenting of (1) claims 1, 2, 6-9, 12, 13, 15, 17-19 and 27 over claims 1, 2,

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and 4-10 of application no. 09/206,208; (2) claims 1, 2, 6-9, 12, 13 and 15-27 over claims 1-14 of application no. 09/206,218; (3) claims 1, 2, 6-9, 12, 13 and 15-27 over claims 9-14 of application no. 09/206,210; and (4) claims 1, 2, 6-9, 12, 13 and 15-27 over claims 1, 2, 4-10, 12-14, 16-20, 22, 24 and 27 of application no. 09/206,216.

Therefore the decision of the examiner to reject the claims on appeal is affirmed.

No time period for taking any subsequent action in connection with this appeal may be extended under 37 CFR § 1.136(a).

**AFFIRMED**

CHARLES F. WARREN	)	
Administrative Patent Judge	)	
	)	
	)	
	)	
	)	BOARD OF PATENT
THOMAS A. WALTZ	)	APPEALS
Administrative Patent Judge	)	AND
	)	INTERFERENCES
	)	
	)	
	)	
ROMULO H. DELMENDO	)	
Administrative Patent Judge	)	



Appeal No. 2002-1863  
Application No. 09/206,207

TAW/jrg

Appeal No. 2002-1863  
Application No. 09/206,207

FINA TECHNOLOGY INC.  
PO BOX 674412  
HOUSTON, TX 77267-4412

The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

Paper No. 23

UNITED STATES PATENT AND TRADEMARK OFFICE

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BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

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Ex parte JEAN-PIERRE DATH, LUC DELORME, JACQUES-FRANCOIS GROOTJANS,  
XAVIER VANHAEREN and WALTER VERMEIREN

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Appeal No. 2002-1864  
Application No. 09/206,208

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HEARD: March 20, 2003

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Before WARREN, WALTZ, and DELMENDO, Administrative Patent Judges.  
WALTZ, Administrative Patent Judge.

**DECISION ON APPEAL**

This is a decision on an appeal from the primary examiner's final rejection of claims 1, 2 and 4 through 12, which are the only claims pending in this application.<sup>1</sup> We have jurisdiction pursuant to 35 U.S.C. § 134.

According to appellants, the invention is directed to a process for the production of olefins by the catalytic cracking of

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<sup>1</sup>An amendment dated July 26, 2001, Paper No. 12, subsequent to the final rejection, has been entered by the examiner as per the Advisory Action dated Aug. 10, 2001, Paper No. 13.

Appeal No. 2002-1864  
Application No. 09/206,208

an olefin-containing feedstock by using a pretreated MFI crystalline catalyst under particular cracking conditions (Brief, pages 2-3). Illustrative independent claim 1 is reproduced below:

1. A process for the catalytic cracking of an olefin-containing feedstock which is selective toward light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing at least one olefin with a MFI crystalline silicate catalyst having a silicon/aluminum atomic ratio from 180 to 1000, which has been obtained by pretreating so as to increase the silicon/aluminum atomic ratio thereof by heating the catalyst in steam to reduce tetrahedral aluminum in the crystalline silicate framework to form alumina and de-aluminating the catalyst by treating the catalyst with a complexing agent for aluminum to remove aluminum from the pores of said crystalline silicate at an inlet temperature of from 500 to 600°C and at an olefin partial pressure of from 0.1 to 2 bars to produce an effluent with an olefin content of lower molecular weight than that of the feedstock.

The examiner has relied upon the following references as evidence of obviousness:

Eberly, Jr., et al. (Eberly)	3,506,400	Apr. 14, 1970
Colombo et al. (EP '060)	0 109 060	May 23, 1984
(published European Patent Application)		

The claims on appeal stand rejected under 35 U.S.C. § 103(a) as unpatentable over EP '060 in view of Eberly (Answer, page 3). The claims on appeal also stand provisionally rejected under the judicial created doctrine of obviousness-type double patenting over (1) claims 1, 2, 5-10, 12, 13 and 15 of copending application

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no. 09/206,207 (Answer, page 4); (2) claims 1-14 of copending application no. 09/206,218 (Answer, page 5); (3) claims 9-14 of copending application no. 09/206,210 (*id.*); and (4) claims 1, 2, 4-10, 12-14, 16-20, 22, 24 and 27 of copending application no. 09/206,216 (Answer, page 6).

We summarily *affirm* all of the examiner's provisional rejections based on obviousness-type double patenting for the reasons stated in the Answer. We *reverse* the examiner's rejection based on section 103(a) essentially for the reasons stated in the Brief, Reply Brief, and those reasons set forth below. Therefore the decision of the examiner to reject the claims on appeal is *affirmed*.

#### OPINION

##### *A. The Rejections based on Obviousness-type Double Patenting*

Appellants do not contest the examiner's provisional rejections based on the judicially created doctrine of obviousness-type double patenting (Brief, pages 4-5). Appellants state their intention of submitting an appropriate terminal disclaimer when one or more of the copending applications listed above issue as a patent (Brief, page 5). Accordingly, we summarily *affirm* all of the examiner's provisional rejections based on the judicially created doctrine of obviousness-type double patenting. See *In re*

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*Wetterau*, 356 F.2d 556, 557-58, 148 USPQ 499, 500-01 (CCPA 1966);  
*Ex parte Karol*, 8 USPQ2d 1771, 1773-74 (Bd. Pat. App. & Int. 1988).

*B. The Rejection based on 35 U.S.C. § 103(a)*

The examiner finds that EP '060 discloses a process for producing olefins by catalytic cracking an olefin feedstock with a zeolitic catalyst such as silicalite or ZSM-5 with a silica/alumina atomic ratio of greater than 175 under reaction conditions encompassing the claimed parameters (Answer, page 3). The examiner recognizes that EP '060 does not disclose, *inter alia*, the claimed pretreatment of the catalyst including steaming and aluminum extraction (*id.*). To remedy this deficiency, the examiner applies Eberly for the disclosure of a process for treating zeolite by steaming followed by contact with a complexing agent to remove aluminum from the gross structure of the zeolite, thereby increasing the silica/alumina ratio (Answer, page 4). From these findings, the examiner concludes that it would have been obvious to one of ordinary skill in the art to modify the process of EP '060 "by dealuminating the zeolite to achieve the desired silicon:aluminum atomic ratio as suggested by Eberly because the resulting zeolite will have higher stability." *Id.*

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Application No. 09/206,208

It is incumbent upon the examiner, when proposing a combination or modification of references, to identify some suggestion to combine the references or make the modification. See *In re Mayne*, 104 F.3d 1339, 1342, 41 USPQ2d 1451, 1454 (Fed. Cir. 1997). As correctly argued by appellants (Brief, pages 7-10; Reply Brief, page 3), Eberly is not directed to MFI-type catalysts and only suggests silica/alumina mole ratios much lower than those required by EP '060 (and much lower than those required in the claims on appeal). Eberly does disclose that the catalysts are useful in cracking processes (col. 1, ll. 64-71, and col. 9, ll. 55-61) and that higher silica/alumina mole ratios provide greater stability to heat, steam and acid (col. 2, ll. 20-25). However, these "higher" silica/alumina mole ratios suggested by Eberly are ones such as 8:1 to 12:1 (col. 2, ll. 25-34), with examples as high as 29:1 (Table IV, col. 8, l. 11). Eberly teaches heating a catalyst in steam, followed by extraction with EDTA, results in a catalyst with an "extremely high" silica/alumina mole ratio of about 20 (see Table III, col. 7, ll. 18-37). The lowest silica/alumina mole ratio suggested by EP '060 is 350 (see EP '060, page 1, and the Answer, page 3, converting this value to an atomic ratio of greater than 175). The examiner has not presented any

convincing reasoning, suggestion or motivation as to why one of ordinary skill in this art would have modified the process of EP '060, with catalysts already possessing silica/alumina atomic ratios of greater than 175, with the catalyst pretreatment of Eberly when Eberly teaches that silica/alumina mole ratios of 8 through 20 provide sufficiently increased stability. Accordingly, we determine that the examiner has not presented convincing reasons for the proposed combination of references and therefore no case of *prima facie* obviousness has been established.<sup>2</sup> Thus we cannot sustain the examiner's rejection based on the combination of EP '060 and Eberly.

C. Summary

The examiner's rejection of claims 1, 2 and 4-12 under 35 U.S.C. § 103(a) over EP '060 in view of Eberly is reversed.

The examiner's provisional rejections of claims 1, 2 and 4-12 based on the judicially created doctrine of obviousness-type double patenting over (1) claims 1, 2, 5-10, 12, 13 and 15 of application no. 09/206,207; (2) claims 1-14 of application no. 09/206,218;

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<sup>2</sup>Since we determine that no case of *prima facie* obviousness has been established, a discussion of appellants' countervailing evidence of non-obviousness (Exhibits B and C attached to the Brief) is unnecessary to this decision.



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(3) claims 9-14 of application no. 09/206,210; and (4) claims 1, 2, 4-10, 12-14, 16-20, 22, 24 and 27 of application no. 09/206,216 are affirmed.

Therefore the decision of the examiner to reject the claims on appeal is affirmed.

No time period for taking any subsequent action in connection with this appeal may be extended under 37 CFR § 1.136(a).

**AFFIRMED**

CHARLES F. WARREN	)	
Administrative Patent Judge	)	
	)	
	)	
	)	
	)	BOARD OF PATENT
THOMAS A. WALTZ	)	APPEALS
Administrative Patent Judge	)	AND
	)	INTERFERENCES
	)	
	)	
	)	
ROMULO H. DELMENDO	)	
Administrative Patent Judge	)	

TAW/jrg

Appeal No. 2002-1864  
Application No. 09/206,208

FINA TECHNOLOGY INC.  
PO BOX 674412  
HOUSTON, TX 77267-4412

The opinion in support of the decision being entered today was **not** written for publication and is **not** binding precedent of the Board.

Paper No. 44

UNITED STATES PATENT AND TRADEMARK OFFICE

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BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

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Ex parte JEAN-PIERRE DATH, LUC DELORME, JACQUES-FRANCOIS  
GROOTJANS, XAVIER VANHAEREN, and WALTER VERMEIREN

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Appeal No. 2005-0183  
Application No. 09/206,218

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HEARD: Feb. 9, 2005

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Before WARREN, WALTZ, and DELMENDO, Administrative Patent Judges.  
WALTZ, Administrative Patent Judge.

**DECISION ON APPEAL**

This is a decision on an appeal from the primary examiner's final rejection of claims 1 through 12, 14, 15, and 18 through 21, which are the only claims remaining in this application. We have jurisdiction pursuant to 35 U.S.C. § 134.

According to appellants, the invention is directed to a process for increasing the stability of a MFI crystalline silicate catalyst where the catalyst is pretreated by steaming followed by de-aluminating through use of a complexing agent for

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aluminum, as well as a process for the production of olefins by catalytic cracking of a hydrocarbon feedstock using these pretreated catalysts (Brief, pages 3-4). A copy of representative independent claim 1 is attached as an Appendix to this decision.

The examiner relies upon the following references as evidence of obviousness:

Eberly, Jr., et al. (Eberly)	3,506,400	Apr. 14, 1970
Colombo et al. (EP '060) (published European Patent Application)	0 109 060	May 23, 1984

Claims 1-12, 14 and 19 stand rejected under 35 U.S.C. § 103(a) as unpatentable over EP '060 in view of Eberly (Answer, page 3). Claims 15, 18, 20 and 21 stand rejected under 35 U.S.C. § 103(a) as unpatentable over Eberly (Answer, page 5). Claims 1-12, 14 and 19 stand provisionally rejected under the judicially created doctrine of obviousness-type double patenting as unpatentable over claims 1, 2, 4-10, 12-14, 16-20, 22, 24 and 27 of co-pending Application No. 09/206,216 (Answer, page 8).<sup>1</sup>

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<sup>1</sup>The examiner also provisionally rejects many of the claims on appeal under the judicially created doctrine of obviousness-type double patenting over the claims of Application Nos. 09/206,207, 206,208, and 206,210 (Answer, pages 6-8). As noted by appellants, these applications have now matured into patents and terminal disclaimers have been submitted (Reply Brief, pages 1-2). The examiner has accepted the terminal disclaimers and  
(continued...)

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Application No. 09/206,218

We *affirm* the examiner's provisional rejection for obviousness-type double patenting essentially for the reasons stated in the Answer. See *Ex parte Karol*, 8 USPQ2d 1771, 1773 (Bd. Pat. App. & Int. 1988) (a provisional rejection may properly be made over rejected claims of a co-pending application). We reverse the examiner's rejections based on prior art under section 103(a) essentially for the reasons stated in the Brief, Reply Brief, and those reasons set forth below. Accordingly, the decision of the examiner is *affirmed-in-part*.

#### OPINION

##### A. *The Obviousness-type Double Patenting Rejection*

The examiner states the findings and conclusion of law with regard to the obviousness-type double patenting rejection over the claims of Application No. 09/206,216 on pages 8-9 of the Answer. Appellants do not dispute or contest the facts or conclusion set forth in this provisional rejection (see the Brief and Reply Brief in their entirety). Appellants note their intention to file an appropriate terminal disclaimer upon

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<sup>1</sup>(...continued)  
therefore the obviousness-type double patenting rejections over each of these applications have been withdrawn (Letter dated July 30, 2004, Paper No. 38). Accordingly, these rejections are not on appeal before this merits panel.

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Application No. 09/206,218

allowance of Application No. 09/206,216 (Brief, page 6).

Accordingly, we summarily affirm the examiner's rejection.

*B. The Rejections under § 103(a)*

The examiner finds that EP '060 discloses a process for producing olefins by catalytic cracking of a hydrocarbon feed using a zeolitic catalyst including silicalite and ZSM-5 with silicon/aluminum atomic ratios equal to or greater than 175 (corresponding to a molar ratio of equal to or greater than 350) (Answer, page 3). The examiner also finds that EP '060 fails to disclose, *inter alia*, that the catalyst has been pretreated to increase the silicon/aluminum ratio and increase the stability of the catalyst (Answer, page 4).

The examiner finds that Eberly discloses a process for treating a zeolite by steaming followed by contact with a complexing agent to remove aluminum from the gross structure of the zeolite thereby increasing the silicon/aluminum ratio of the zeolite (*id.*). From these findings, the examiner concludes that it would have been obvious to one of ordinary skill in the art at the time of appellants' invention to have modified the process of EP '060 "by dealuminating the zeolite to achieve the desired silicon:aluminum atomic ratio as suggested by Eberly because the resulting zeolite will have higher stability" (Answer, page 5).

With regard to the rejection of claims 15, 18, 20 and 21 over Eberly alone, the examiner makes the same findings from Eberly as discussed above (Answer, paragraph bridging pages 5-6). The examiner recognizes that Eberly does not disclose any treatment of a MFI crystalline silicate as claimed by appellants, nor does the reference disclose a post-treatment silicon:aluminum atomic ratio of at least 180 (Answer, page 6).<sup>2</sup> The examiner concludes that it would have been obvious to one of ordinary skill in the art to treat MFI crystalline silicates in the process of Eberly since Eberly does not limit the process to any specific zeolite (Answer, page 6). The examiner also concludes that it would have been obvious to one of ordinary skill in the art to treat a zeolite with any silica:alumina ratio since Eberly discloses treating zeolites having "extremely high" silica:alumina ratios, including ratios greater than 20, as well as disclosing several examples where the treated zeolites "are essentially free of alumina" (*id.*).

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<sup>2</sup>Claims 15, 18, 20 and 21 require a silicon:aluminum atomic ratio of at least 300 (e.g., see claim 15 on appeal). Therefore we presume the examiner mistakenly states that a ratio of "at least 180" would have been obvious in view of Eberly, but meant to state a ratio of "at least 300." However, this error is moot in view of our disposition of the rejections *infra*.

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The initial burden of establishing a *prima facie* case of obviousness rests with the examiner. See *In re Oetiker*, 977 F.2d 1443, 1445, 24 USPQ2d 1443, 1444 (Fed. Cir. 1992). Whether employing a single reference or a combination of references to establish *prima facie* obviousness, the examiner must show evidence that any proposed modification would have been desirable to those of ordinary skill in the art. See *B.F. Goodrich Co. v. Aircraft Braking Sys. Corp.*, 72 F.3d 1577, 1582, 37 USPQ2d 1314, 1318 (Fed. Cir. 1996); *In re Gordon*, 733 F.2d 900, 902, 221 USPQ 1125, 1127 (Fed. Cir. 1984). "[T]here must be some logical reason apparent from positive, concrete evidence of record which justifies a combination of primary and secondary references." See *In re Regel*, 526 F.2d 1399, 1403 n.6, 188 USPQ 136, 139 n.5 (CCPA 1975).

As correctly argued by appellants (Brief, page 10; Reply Brief, page 4), the examiner has not presented any convincing reasoning, suggestion or motivation as to why one of ordinary skill in this art would have modified the process of EP '060, where the catalyst already possess silicon:aluminum atomic ratios of greater than 175, with the catalyst pretreatment of Eberly, where Eberly teaches that silica:alumina mole ratios of up to 29 (i.e., atomic ratios of up to 14.5) provide sufficiently



increased stability to the zeolite catalyst. Similarly, with regard to the rejection over Eberly alone, the examiner has not presented any convincing reasoning, suggestion or motivation as to why one of ordinary skill in this art would have employed the pretreatment taught by Eberly to MFI crystalline silicate catalysts to yield silicon/aluminum atomic ratios of from 300 to 1000.

As also correctly argued by appellants (Brief, pages 7-8; Reply Brief, page 2), Eberly does not disclose pretreatment of the MFI crystalline silicate catalysts required by all the claims on appeal. Eberly discloses pretreatment of "crystalline aluminosilicate zeolites of the molecular sieve type" in general having the formula recited at col. 2, ll. 3-4 (see also col. 1, ll. 34-35). The value of X in this formula requires silica:alumina mole ratios of 1.5 to 12 (i.e., atomic ratios of 0.75 to 6; see col. 2, ll. 7-8). Eberly further teaches the use of many natural and synthetic zeolites, none of which has been identified by the examiner as a MFI crystalline silicate catalyst (col. 2, ll. 9-18).

Eberly teaches "extremely high" silica:alumina mole ratios of "15 to 1 or greater" with an example of an "extremely high" mole ratio of 29 (col. 4, ll. 35-38; col. 7, ll. 35-37; col. 7,

11. 74-75; and Table IV in col. 8). As correctly noted by appellants (Reply Brief, pages 2-3), Examples 3 and 4 of Eberly disclose a catalyst "essentially free" of alumina (see also Example 6) but do not disclose or suggest any pretreatment other than that previously used to produce silica:alumina molar ratios of up to 29. Therefore we agree with appellants that the silicon:aluminum atomic ratios required by the claims on appeal would not have been suggested as desirable by Eberly since the much lower values taught by Eberly gave the desired catalyst stability.

For the foregoing reasons and those stated in the Brief and Reply Brief, we determine that the examiner has not established a *prima facie* case of obviousness in view of the reference evidence. Therefore we need not consider the sufficiency of appellants' evidence of non-obviousness (Brief, pages 13-14). See *In re Geiger*, 815 F.2d 686, 688, 2 USPQ2d 1276, 1278 (Fed. Cir. 1987). Accordingly, the rejections on appeal based on section 103(a) cannot be sustained.

C. Summary

The provisional rejection of claims 1-12, 14 and 19 under the judicially created doctrine of obviousness-type double

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Application No. 09/206,218

patenting over claims 1, 2, 4-10, 12-14, 16-20, 22, 24, and 27 of  
co-pending Application No. 09/206,216 is affirmed.

The rejection of claims 1-12, 14 and 19 under 35 U.S.C.  
§ 103(a) over EP '060 in view of Eberly is reversed. The  
rejection of claims 15, 18, 20 and 21 under 35 U.S.C. § 103(a)  
over Eberly is also reversed.

The decision of the examiner is affirmed-in-part.

No time period for taking any subsequent action in  
connection with this appeal may be extended under 37 CFR  
§ 1.136(a)(1)(iv) (effective Sep. 13, 2004; 69 Fed. Reg. 49960  
(Aug. 12, 2004); 1286 Off. Gaz. Pat. Office 21 (Sep. 7, 2004)).

**AFFIRMED-IN-PART**

Charles F. Warren	)	
Administrative Patent Judge	)	
	)	
	)	
	)	
	)	BOARD OF PATENT
Thomas A. Waltz	)	APPEALS
Administrative Patent Judge	)	AND
	)	INTERFERENCES
	)	
	)	
	)	

Appeal No. 2005-0183  
Application No. 09/206,218

Romulo H. Delmendo                    )  
Administrative Patent Judge        )

TAW/tdl

Appeal No. 2005-0183  
Application No. 09/206,218

Fina Technology Inc.  
P.O. Box 674412  
Houston, TX 77267-4412

**APPENDIX**

1. A process for the production of olefins by catalytic cracking, the process comprising feeding a hydrocarbon feedstock containing at least one olefin of C<sub>4</sub> or greater over an MFI crystalline silicate catalyst to produce an effluent containing at least one olefin of C<sub>2</sub> or greater by catalytic cracking which is selective towards light olefins in the effluent, whereby for increasing the catalyst stability by limiting formation of coke thereon during the cracking process the catalyst has a silicon/aluminum atomic ratio of from 300 to 1000, the olefin partial pressure is from 0.1 to 2 bars, and the feedstock contacts the catalyst at an inlet temperature of from 500 to 600°C, wherein the catalyst has been pretreated by heating the catalyst in steam to reduce the tetrahedral aluminum in the crystalline silicate framework of said catalyst and convert the tetrahedral aluminum to octahedral aluminum in the form of amorphous alumina causing partial obstruction in the pores of said crystalline silicate framework and thereafter dealuminating the catalyst by treating the catalyst with a complexing agent for aluminum to remove amorphous alumina from the pores of said crystalline silicate framework and at least partially recover the micropore volume to increase the silicon/aluminum atomic ratio of the catalyst to a value of from 300 to 1000.

The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

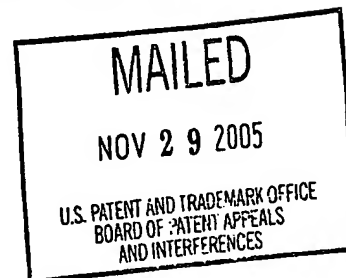
UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

Ex parte JEAN-PIERRE DATH, LUC DELORME, JACQUES-FRANCOIS  
GROOTJANS, XAVIER VANHAEREN and WALTER VERMEIREN

Appeal No. 2005-2371  
Application No. 09/206,216

HEARD: OCTOBER 19, 2005



Before GARRIS, WARREN, and WALTZ, Administrative Patent Judges.  
WALTZ, Administrative Patent Judge.

**DECISION ON APPEAL**

This is a decision on an appeal from the primary examiner's refusal to allow claims 17 through 20 and 38 through 44, the only claims pending in this application, as amended subsequent to the final rejection (see the amendment filed with the Brief, entered as noted on page 2, ¶(4), of the Answer; see also the Brief, pages 1-2). We have jurisdiction pursuant to 35 U.S.C. § 134.

According to appellants, the invention is directed to a process for the cracking of olefins in an olefin-rich feedstock

where the feedstock has been treated by selective hydrogenation to remove dienes and the cracking is accomplished under specific conditions using an MFI crystalline silicate catalyst having a silicon/aluminum atomic ratio of from 180 to 1000 (Brief, page

3). Representative independent claim 17 is reproduced below:

17. A process for cracking an olefin-rich hydrocarbon feedstock which is selective towards propylene in the effluent, the process comprising contacting a hydrocarbon feedstock having a maximum diene concentrated therein of 0.1 wt.% containing olefins having a first composition of at least one olefinic component with an MFI crystalline silicate catalyst having a silicon/aluminum atomic ratio of from 180 to 1000 to produce an effluent having a second composition of at least one olefinic component, the feedstock contacting the catalyst at an inlet temperature of from 500 to 600°C and being passed over the catalyst at an LHSV of from 10 to 30h<sup>-1</sup>, the feedstock and the effluent having substantially the same olefinic content by weight therein, and the effluent having a higher propylene content than the feedstock, wherein the dienes have been removed from the feedstock prior to the cracking step by selective hydrogenation.

The examiner has relied upon the following references as evidence of obviousness:

Glockner et al. (Glockner)	4,078,011	Mar. 07, 1978
Cosyns et al. (Cosyns)	4,347,392	Aug. 31, 1982
Colombo et al. (EP '060) (published European Patent Application)	0 109 060	May 23, 1984

Claims 17 through 20 stand provisionally rejected under the judicially created doctrine of obviousness-type double patenting over claims 1 through 16 of copending Application No. 09/206,218



(Answer, page 3).<sup>1</sup> Claims 17-20 and 38-44 stand rejected under 35 U.S.C. § 103(b) as unpatentable over EP '060 in view of either Glockner or Cosyns (*id.*).<sup>2</sup>

Based on the totality of the record, including the opposing arguments in the Brief, Reply Brief, and the Answer, we reverse the examiner's rejection of claims 17-20 and 38-44 under section 103 essentially for the reasons stated in the Brief and Reply Brief, as well as those reasons set forth below. Since appellants have not contested or disputed the examiner's provisional rejection for obviousness-type double patenting, we summarily affirm this rejection.<sup>3</sup> Accordingly, the examiner's

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<sup>1</sup>We note that Application No. 09/206,218 was the subject of an appeal (Appeal No. 2005-0183), and a decision affirming-in-part the examiner's rejection was mailed on Feb. 25, 2005 (Paper No. 44). We further note that Application No. 09/206,218 issued on Oct. 4, 2005, as U.S. Patent No. 6,951,968, and thus this rejection is not now "provisional."

<sup>2</sup>Since it is clear that section 103(b) is not applicable in this rejection, we presume for purposes of this appeal that the examiner meant to use section 103(a) as the statutory basis for the rejection. We also note that the final Office action mistakenly listed 35 U.S.C. § 102(b) as the statutory basis for this rejection but it is clear from the record that appellants and the examiner understood this rejection to be based on obviousness under section 103 (Brief, page 5, "Issues;" final Office action dated Oct. 31, 2003, pages 3-6, especially page 3 reproducing section 103(a) of the statute). Accordingly, for purposes of this appeal, we consider this rejection as based on 35 U.S.C. § 103(a).

<sup>3</sup>Appellants' attorney, at the oral hearing on Oct. 19, 2005, acknowledged that the Brief and Reply Brief did not mention this provisional rejection but assumed that a terminal disclaimer had been filed which would obviate this rejection. Upon review of the image file wrapper, we find no terminal disclaimer over Application No. 206,218.

decision to reject the claims on appeal is *affirmed-in-part*.

#### OPINION

*A. The Provisional Rejection for Obviousness-type Double  
Patenting*

As discussed above, the examiner repeats this provisional rejection on page 3 of the Answer and appellants do not contest or dispute this rejection in either the Brief or Reply Brief (see the Brief and Reply Brief in their entirety). Accordingly, we summarily affirm the examiner's provisional rejection.

*B. The Rejection under § 103(a)*

The examiner finds that EP '060 discloses a process of cracking a hydrocarbon feed of C4 to C12 olefins into propylene and some ethylene by contacting the feed with a crystalline alumino-silicate catalyst having a silicon/alumina atomic ratio of greater than 175 while under reaction conditions which overlap the claimed values (Answer, page 4). The examiner recognizes that EP '060 does not specifically disclose that the feed contains dienes, nor discloses the hydrogenation of any dienes (Answer, page 5). Therefore the examiner applies Glockner or Cosyns for the teaching of processes for the selective hydrogenation of dienes from a hydrocarbon feedstock (*id.*). From

these findings, the examiner concludes that it would have been obvious to one of ordinary skill in this art at the time of appellants' invention "to have modified the EP 0109060 process by including a selective hydrogenation as disclosed by either Glockner or Cosyns because the EP process does not require the presence of dienes" and one of ordinary skill in the art would have looked to remove dienes by the prior art processes of Glockner or Cosyns "if such compounds are not desired" (*id.*). The examiner further finds that

Even if the feedstock of Columbo comprises dienes, one of skill in the art would employ a well known hydrogenation process of either Glockner or Cosyns to remove dienes from the olefinic feedstock because it is well known that a large amount of dienes contained in an olefinic feedstock would depress [sic] the overall cracking conversion and/or selectivity of the process. Answer, paragraph bridging pages 6-7, italics added.

The initial burden of establishing a prima facie case of obviousness in view of prior art references rests with the examiner. See *In re Oetiker*, 977 F.2d 1443, 1445, 24 USPQ2d 1443, 1444 (Fed. Cir. 1992). Even though individual elements of a claimed invention may be well known, "the question is whether there is something in the prior art as a whole to suggest the desirability, and thus the obviousness, of making the combination.". *Lindemann Maschinenfabrik GMBH v. American Hoist*

& *Derrick Co.*, 730 F.2d 1452, 1462, 221 USPQ 481, 488 (Fed. Cir. 1984); see also *In re Gordon*, 733 F.2d 900, 902, 221 USPQ 1125, 1127 (Fed. Cir. 1984). "[T]here must be some logical reason apparent from positive, concrete evidence of record which justifies a combination of primary and secondary references." *In re Regel*, 526 F.2d 1399, 1403 n.6, 188 USPQ 136, 139 n.6 (CCPA 1975).

Here we determine that the examiner has not met the initial burden of establishing a case of prima facie obviousness in view of the prior art references. The examiner's finding that EP '060 does not address the subject of dienes in the feedstock (Answer, page 5; Brief, page 6) does not provide any positive teaching to remove dienes if they were found to be present in a feedstock of the same or similar process, since there is no evidence on this record that dienes would have been undesirable in the feedstock of EP '060. Furthermore, the examiner has not presented any findings of fact that Glockner or Cosyns is directed to the selective hydrogenation of dienes in the same or similar feedstock used in the conversion of higher olefins into propylene as disclosed by the process of EP '060. Glockner teaches removal of dienes from an olefin stream employed in standard alkylation processes (col. 1, ll. 7-19). Cosyns teaches removal of diene

and triene impurities in the production of pure ethylene or propylene (col. 1, ll. 7-9 and 30-32). Finally, as correctly argued by appellants (Reply Brief, page 2), the examiner has provided no factual evidence to support the contention that it was "well known" that a large amount of dienes would depress the overall cracking conversion and selectivity of the process of EP '060 (Answer, pages 6-7). See *In re Lee*, 277 F.3d 1338, 1344-45, 61 USPQ2d 1430, 1434-35 (Fed. Cir. 2002). Therefore the examiner has not established the desirability of removing dienes from the olefin feedstock in the cracking process of EP '060.

For the foregoing reasons and those stated in the Brief and Reply Brief, we determine that the examiner has not established a *prima facie* case of obviousness in view of the reference evidence. Therefore we cannot sustain the examiner's rejection of the claims on appeal under 35 U.S.C. § 103(a) over EP '060 in view of Glockner or Cosyns.

C. Summary

The provisional rejection of claims 17-20 under the judicially created doctrine of obviousness-type double patenting over claims 1-16 of Application No. 09/206,218 is affirmed.

The rejection of claims 17-20 and 38-44 under 35 U.S.C. § 103(a) over EP '060 in view of Glockner or Cosyns is reversed.


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The decision of the examiner is affirmed-in-part.

No time period for taking any subsequent action in connection with this appeal may be extended under 37 CFR § 1.136(a)(1)(iv)(2004).

**AFFIRMED-IN-PART**

BRADLEY R. GARRIS  
Administrative Patent Judge

  
CHARLES F. WARREN  
Administrative Patent Judge

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THOMAS A. WALTZ  
Administrative Patent Judge

TW/rwk

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FINA TECHNOLOGY INC  
PO BOX 674412  
HOUSTON, TX 77267-4412

F 758

The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

Paper No. 20

## UNITED STATES PATENT AND TRADEMARK OFFICE

DOCKETED:

*Reconsideration*  
Date due: 5/31/04

BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

Ex parte JEAN-PIERRE DATH and WALTER VERMEIREN



Appeal No. 2004-0988  
Application No. 09/596,356

ON BRIEF

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Before WARREN, WALTZ, and DELMENDO, Administrative Patent Judges.  
WALTZ, Administrative Patent Judge.

## DECISION ON APPEAL

This is a decision on an appeal from the primary examiner's final rejection of claims 1 through 9, which are the only claims pending in this application.<sup>1</sup> We have jurisdiction pursuant to

<sup>1</sup>Appellants submitted an amendment subsequent to the final rejection which was refused entry by the examiner (see the amendment dated June 17, 2002, Paper No. 11, refused entry as per the Advisory Action dated June 24, 2002, Paper No. 12; Brief, page 2). Appellants further submitted an amendment with the Brief to change the dependency of claim 6 (see the amendment dated Dec. 23, 2002, with no Paper No.; Brief, pages 2-3). Although the examiner indicates that he "agrees" with the amendment (Answer, page 2, ¶(4)), this amendment has not been noted on the record as entered and has not been physically entered in the file record. Accordingly, we consider the claims  
(continued...)



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35 U.S.C. § 134.

According to appellants, the invention is directed to a process for the catalytic cracking of an olefin-rich feedstock using a MEL-type crystalline silicate catalyst which has a silicon/aluminum atomic ratio within the range of 150-800 and has been subjected to steaming in order to produce an effluent with an olefin content of lower molecular weight than that of the feedstock (Brief, page 3). Appellants state that the claims do not stand or fall together (Brief, page 5). To the extent appellants present specific, substantive separate arguments for dependent claims (Brief, pages 11-13), we consider these claims separately. See *In re McDaniel*, 293 F.3d 1379, 1383, 63 USPQ2d 1462, 1465 (Fed. Cir. 2002). Representative independent claim 1 is reproduced below:

1. A process for the catalytic cracking of an olefin-rich feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing one or more olefins, with an MEL crystalline silicate catalyst, which has been subjected to a steaming step and has a silicon/aluminum atomic ratio of from 150 to 800, at an inlet temperature of from 500 to 600°C, at an olefin partial pressure of from 0.1 to 2 bars and the feedstock being passed over the catalyst at an LHSV of from 10 to 30h<sup>-1</sup>, to produce an effluent with an olefin content of lower molecular weight than that of the feedstock.

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<sup>1</sup>(...continued)  
as they are found in the file record, i.e., as presented as of the final Office action.

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The examiner relies upon the following references as evidence of obviousness:

Haag et al. (Haag)	0 034 444	Aug. 26, 1981
(published European Patent Application)		

Colombo et al. (Colombo)	0 109 060	May 23, 1984
(published European Patent Application)		

The claims on appeal stand rejected under 35 U.S.C. § 103(a) as unpatentable over Colombo in view of Haag (Answer, page 3). We *affirm* the examiner's rejection essentially for the reasons stated in the Answer and those reasons set forth below.

#### OPINION

The examiner finds that Colombo discloses a process of cracking a feedstock containing C4 to C12 olefins in the presence of a MEL crystalline silicate catalyst (e.g., ZSM-11) having a silicon/aluminum atomic ratio of at least 175 (i.e., 350/2) under reaction conditions of a temperature from 400 to 600°C. and a space velocity ranging from 5 to 200 hr<sup>-1</sup> to produce lower olefins, namely propylene (Answer, page 3). The examiner recognizes that Colombo fails to disclose two limitations recited in claim 1 on appeal, namely the pretreatment of the catalyst with steam and the olefin partial pressure (*id.*). However, the examiner finds that Colombo discloses that the conversion of feedstock may benefit from activating the catalyst as taught by Haag, where Haag teaches

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steaming the catalyst for a sufficient time, temperature, and water partial pressure (*id.*). The examiner also finds that the olefin partial pressures may be calculated from the examples of Colombo and such calculated olefin partial pressures fall within the claimed range (Answer, page 4). The examiner further finds that Colombo teaches that the behavior of silicalites such as ZSM-11 depends on the conversion pressure (*id.*). From these findings, the examiner concludes that it would have been obvious to one of ordinary skill in this art at the time the invention was made to have activated the catalyst of Colombo by steaming, as taught by Haag, for optimal activity (Answer, page 3). We agree.

Appellants argue that Haag is "devoid of any disclosure respecting the cracking of an olefin feedstock to produce an effluent having a lower molecular weight." Brief, sentence bridging pages 5-6. This argument is not well taken since Haag specifically teaches that his steam activated catalysts "have extremely high cracking activity" and may be used to convert olefins from high to low molecular weight substances (Haag, page 21, ll. 12-15). Haag further teaches the cracking conditions applicable to the steam activated catalysts, all of which overlap the conditions recited in claim 1 on appeal (Haag, page 23, ll. 5-15).

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Appellants argue that the teaching in Colombo to use the "initial activation" of Haag actually refers to the initial activation by heating in an inert atmosphere followed by a base exchange with ammonium salts taught by Haag, not a treatment of the catalyst with steam (Brief, page 6). This argument is not persuasive since it is clear from Colombo (page 3, ll. 9-13) and Haag (page 11, ll. 21-27) that the activation of the catalyst by heating and base exchange merely renders the catalyst active and in the correct (hydrogen or acidic) form for the steam treatment to increase the activity (Haag, page 14, ll. 22-29, and page 17, ll. 17-18).

Appellants argue that Haag teaches steaming zeolites of relative low Si/Al ratios and discloses a "wide variety" of reactions, some of which involve olefins (Brief, page 7). From the examples of Haag, appellants calculate the highest Si/Al ratio used was about 45 (Brief, page 8). Therefore appellants argue that one of ordinary skill in the art, viewing only Haag and Colombo, would not attempt to apply the steaming procedure in Haag to MEL silicates of much higher Si/Al ratios (*id.*).

Appellants' arguments are not persuasive. Haag specifically teaches use of the steamed catalyst in cracking of olefins (page 21, ll. 12-15). Haag also teaches application of the steaming

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procedure to catalysts with Si/Al ratios inclusive of the claimed ranges (Haag, page 4, ll. 2-5; page 6, ll. 22-24), and teaches that the catalysts include MEL silicates such as ZSM-11 (e.g., Haag, page 11, ll. 1-3). Colombo, as discussed above, similarly teaches use of MEL silicates such as ZSM-11 with Si/Al ratios within the claimed range. We note that a reference is not limited to its examples but is available for all that it discloses and suggests to one of ordinary skill in the art. See *In re Widmer*, 353 F.2d 752, 757, 147 USPQ 518, 523 (CCPA 1965).

Appellants argue that Colombo does not disclose or suggest the particular combination of parameters recited in claim 1 on appeal but instead discloses very broad ranges of Si/Al ratio, olefin partial pressure, space velocity and temperature (Brief, page 8). This argument is not well taken since the ranges of parameters disclosed by Colombo overlap or include the ranges of parameters recited in claim 1 on appeal, thus rendering the claimed ranges obvious absent a showing of criticality. See *In re Woodruff*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

For the foregoing reasons and those stated in the Answer, we determine that the examiner has established a *prima facie* case of obviousness in view of the reference evidence. Appellants argue that the data presented in the Examples of the specification

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clearly shows unexpected results (Brief, pages 10-12).

Accordingly, we begin anew and review the totality of the evidence for and against obviousness. See *In re Oetiker*, 977 F.2d 1443, 1445, 24 USPQ2d 1443, 1444 (Fed. Cir. 1992).

Appellants present data from Examples 1-3 (Figures 1-3) to show a sustained period of high propylene yield for the MEL catalyst as compared to corresponding catalysts which have not been steamed (Comparative Examples 1 and 2 (Figures 4-5)) or have high Si/Al ratios (Comparative Example 3 (Figure 6)) (Brief, pages 10-11). We do not find these results persuasive for several reasons. First, steam pretreatment of a ZSM-11 catalyst used in cracking of olefins would have been expected to yield beneficial results, as taught by Haag (see the Answer, page 5). See *In re Skoll*, 523 F.2d 1392, 1397, 187 USPQ 481, 484 (CCPA 1975); *In re Skoner*, 517 F.2d 947, 950, 186 USPQ 80, 82 (CCPA 1975) (expected beneficial results are evidence of obviousness just as unexpected beneficial results are evidence of unobviousness). Second, the results are not commensurate in scope with the subject matter sought to be patented. See *In re Boesch*, 617 F.2d 272, 276, 205 USPQ 215, 219 (CCPA 1980). The examples show steam pretreatment of a ZSM-11 catalyst under specific conditions, followed by treatment with an aluminum scavenger (EDTA) and an ion exchange (e.g., see Example 1

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on pages 21-23 of the specification), while the claims are not so limited, merely reciting a "MEL crystalline silicate catalyst" and "a steaming step" (see claim 1 on appeal). Finally, we note that a comparison, to be effective, must fix all variables except the one sought to show non-obviousness. See *In re Dunn*, 349 F.2d 433, 439, 146 USPQ 479, 483 (CCPA 1965). See Table 2 on page 33 of the specification, where the yield and selectivity are shown at varying times on stream.

Appellants argue that claims 6 and 7 are clearly supported by results commensurate in scope with the claims (Brief, page 11). This argument is not persuasive since, as discussed above, these claims do not further limit the broad recitation of the catalyst and steaming procedure as recited in claim 1 on appeal.

With respect to claims 7-9, appellants argue that Colombo discloses propylene yields substantially less than 30% (Brief, pages 12-13). This argument is not persuasive. The examiner has calculated the amount and yield of propylene from the examples of Colombo (Answer, page 4). Additionally, the yield of propylene disclosed by Colombo would have been expected to increase after the steam pretreatment of the catalyst as taught By Haag.

Based on the totality of the record, including due consideration of appellants' evidence and arguments, we determine

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that the preponderance of evidence weighs most heavily in favor of obviousness within the meaning of section 103(a). Accordingly, we affirm the examiner's rejection of claims 1-9 under 35 U.S.C.

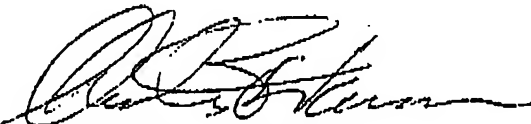
§ 103(a) over Colombo in view of Haag.



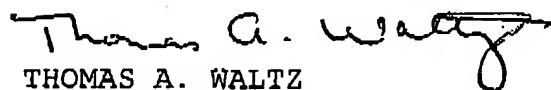
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No time period for taking any subsequent action in connection  
with this appeal may be extended under 37 CFR § 1.136(a).

**AFFIRMED**

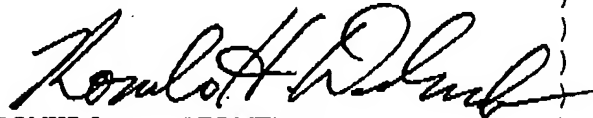


CHARLES F. WARREN  
Administrative Patent Judge



THOMAS A. WALTZ  
Administrative Patent Judge

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ROMULO H. DELMENDO  
Administrative Patent Judge

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FINA TECHNOLOGY INC  
PO BOX 674412  
HOUSTON, TX 77267-4412

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